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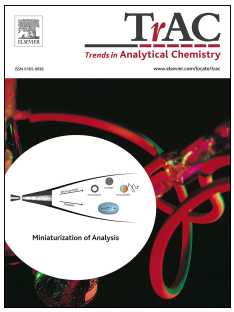

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Miniaturised air sampling techniques for analysis of volatile organic compounds in air

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Abstract

Growing concern about the effects of atmospheric pollutants on climate and human health has accelerated the development of novel analytical methods, including sampling systems, for the determination of atmospheric volatile organic compounds (VOCs). Miniaturised air sampling (MAS) techniques have attracted wide attention in the past two decades due to their advantages (ease of operation, time-integrated sampling, small/no organic solvent consumption, and potential for automation). This review focuses on the latest developments in these techniques, including needle trap microextraction (NTME), in-tube extraction (ITEX), sorption trap, solid-phase microextraction (SPME fibre, SPME Arrow, and retracted SPME fibre), thin-film microextraction (TFME), solid-phase dynamic extraction (SPDE), and stir bar sorptive extraction (SBSE). Further, their benefits, drawbacks, and applicability to air sampling are discussed. The applications of MAS techniques for the analysis of atmospheric air, indoor air, breath air, and emissions of plants and foods are summarised and discussed.

Keywords: Miniaturised air sampling; Volatile organic compounds; Air analysis; Active sampling; Passive sampling; Needle trap microextraction; In-tube extraction; Sorption trap; Solid-phase microextraction; Thin-film microextraction; Solid-phase dynamic extraction; Stir bar sorptive extraction

Abbreviations			
AAS	Active air sampling	PAS	Passive air sampling
BPA	Bisphenol-A	PDMS	Polydimethylsiloxane
BTEX	Benzene, toluene, ethylbenzene, and xylene	REMPI	Resonance enhanced multiphoton ionization
CAR	Carboxen	SBSE	Stir bar sorptive extraction
CWR	Carbon wide range	SIM	Selected ion monitoring
DVB	Divinylbenzene	SMEAR II	Station for Measuring Ecosystem-Atmosphere Relations II
FID	Flame ionization detector	SPDE	Solid-phase dynamic extraction
GC	Gas chromatography	SPME	Solid-phase microextraction
IMS	Ion mobility spectrometry	SVOC	Semivolatile organic compound
ISTD	Internal standard	TD	Thermal desorption
ITEX	In-tube extraction	TDU	Thermal desorption unit
LOD	Limit of detection	TFME	Thin-film microextraction
MAAS	Miniaturised active air sampling	ToF	Time-of-flight
MAS	Miniaturised air sampling	TP	Titanium phosphate
MOF	Metal organic framework	TWA	Time-weighted average
MPAS	Miniaturised passive air sampling	VOC	Volatile organic compound
MS	Mass spectrometry	VVOC	Very volatile organic compound
NTME	Needle trap microextraction	ZIF	Zeolitic imidazolate framework
NTD	Needle trap device		

43

1. Why do we need air analysis?

Growing global concern about the effects of atmospheric pollutants on climate and human health has accelerated the development of novel analytical methods for the determination of volatile organic compounds (VOCs) in the atmosphere. In particular, qualitative and/or quantitative analysis of target compounds in the air increases understanding of their involvement and interlinks with human and environmental toxicology, chemical and biological features, and diseases across different sciences, e.g., environmental science, food science, and biological science. [1-8]. In addition, air analysis provides useful information for authorities regarding legal and regulatory actions and promotes the amendment and adjustment of further actions [1-8]. In addition to aerosol particles, the substances that need to be monitored usually include VOCs, semivolatile organic compounds (SVOCs), chemical precursors (e.g., ozone and nitrogen oxides), and/or different reaction products (like oxidation products). Due to their important role in the environment, this review focuses on the air sampling techniques of VOCs.

VOCs are defined as, "chemicals that have boiling points from 50–260 ^{o}C measured at a standard atmospheric pressure of 101.3 kPa and capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight" [8-9]. The troposphere is the largest source of these volatiles [10] and industrial, agricultural, and social activities are the main emitters of anthropogenic VOCs. Biogenic VOCs, dominated by vegetation and tropical woodlands, crop lands and other woodlands, contribute 60–70% of total VOC emissions [11]. Broad leaf trees and conifer plants emit some highly reactive VOCs, e.g., terpenes, semiterpenes, diterpenes, and isoprene. Most anthropogenic emissions are toxic and have short- or long-term adverse effects on human health and comfort [10]. Benzene and some of its derivatives, e.g., BTEX compounds (benzene, toluene, ethylbenzene, and xylene), are the dominant VOCs in urban areas and comprise approximately two thirds of urban VOCs [12]. They are therefore considered as markers to evaluate air pollution and ambient air quality. In addition to the direct harmful effect VOCs have on humans by triggering different disease and physiological disorders, VOCs indirectly affect our life by altering the Earth's atmosphere, resulting in climate change, stratospheric ozone depletion, acid deposition, photochemical air pollution (smog), and other effects [10-12]. Even though the total quantity of VOCs emitted into the atmosphere annually is large, their concentrations are still at a low, ppt-ppb level, that changes with time [12].

Indoor air quality can have a sizeable impact on human health and well-being as people spend ~70–90% of their lifetime indoors [13]. Building materials, consumer products, smoking, and indoor cooking can release tremendously toxic VOCs into the indoor environment and affect human health by skin penetration and inhalation [9, 13-14]. Even though the association between the concentrations of VOCs and indoor climate complaints is not straightforward, the toxicity of some VOCs, e.g., formaldehyde and BTEX, to residents' health is beyond doubt. Therefore, the recommended VOC levels in indoor air should be kept as low as is reasonably achievable from a health, comfort and sustainability point of view.

The U.S. Food and Drug Administration has approved several breath tests for clinical use. For example, exhaled nitrile oxide is related to asthma and airway inflammation, and alkanes to heart transplant rejection [15]. Breath air analysis provides an alternative to invasive methods and has many benefits, such as less strenuous sampling for subjects, elimination of potential contaminants

and infections, and unlimited quantities of breath gas from patients [2-5]. Early diagnosis of cancer by creating a VOC's profile in the exhaled breath of patients has been widely studied in recent decades [2-4].

Measurement of VOCs emitted by food is useful to obtain information related to food quality, flavour and bio-information, and to avoid food spoilage. The storage and shelf life of food can be determined by evaluating the variation of its emitted VOCs. Identification and quantitation of the key flavour VOCs helps to create food that is more stable with the desired flavours [6, 16-19]. Further, some VOCs can be used as indirect markers of food contamination and spoilage.

In general, the abovementioned types of air contains VOCs, particulate matter, water, nitrogen, oxygen, carbon dioxide, and other inert gases. Among them, VOCs cover only a small fraction and their concentrations are low. Direct measurement by mass spectrometer (MS) or sensors is nowadays available, but in most cases sampling is still an indispensable procedure before instrumental detection [1, 20]. Up to now, air sampling with a wide range of techniques and configurations has been rapidly developed and exploited for different purposes: research, clinical tests, and local-, regional-, or global-scale monitoring [21-23]. The desired air sampling technique should be efficient and meet the requirements set for VOCs by researchers and users.

2. Conventional air sampling techniques and configurations

Conventional air sampling techniques can be classified into two categories: active and passive. Since the early 1970s, active air sampling (AAS) techniques, such as sorbent-packed tubes, have been considered the most accurate ways to measure VOC concentrations in air. These exploit a pump or vacuum to force analytes present in the air to flow through a sampler [7]. The sampler can be a trap, such as a tube packed with a bed or multibed of sorbents, for example polyurethane foam (PUF), XAD resin, active carbon, a porous polymer, or graphitised carbon black [1,7]. Because of the exhaustive characteristic of AAS techniques, analyte concentrations can be easily calculated by referring the instrumental response of the analytes to the pre-constructed calibration curve and then dividing by the total sample volume/mass. Atmospheric conditions, e.g., wind speed, ambient pressure, and humidity, have almost negligible effects on AAS techniques [7]. Conventional air samplers enable VOCs to be tracked at the sub-pptv level, but they are limited by their severe carryover, high cost, and large bulk size which lowers the sampling flexibility in remote areas [24].

Compared to AAS techniques, passive air sampling (PAS) techniques, which normally use a sorbent-coated disk, have a long history originating from 1927 [21]. The difference in chemical potential of the analyte between the sampler and air is the driving force for PAS, either by permeation or diffusion [21, 22]. The biggest advantage of PAS is that it is not reliant on electricity and is therefore especially suitable for time-weighted average (TWA) sampling in remote regions, e.g., forests, mountains, valleys, and wetland. In the customer market, the most used format is the disk sampler [7]. The limiting factor for PAS techniques is the difficulty for quantitation. According to Fick's first law of diffusion, the mass of analyte adsorbed/absorbed by the sorbent material is determined by different conditions, e.g., ambient temperature, analyte concentration, sampling time, and the affinity between the sorbent material and analytes. Furthermore, air pressure and humidity are also important parameters in quantitation.

3. Miniaturised air sampling techniques

During the last two decades, miniaturised air sampling (MAS) techniques have been more frequently employed. These have several benefits, including easy operation, short sampling times, small sampling volumes, small/no organic solvent consumption, automation of analytical operations, and on-line coupling with analytical instruments. In this article, miniaturised AAS (MAAS) and PAS (MPAS) techniques are reviewed. For separation and detection, one- and two-dimensional gas chromatography (GC) coupled with MS, e.g., single quadrupole and time-of-flight (ToF), have been most widely used.

3.1. Miniaturised active air samplers

The most widely used MAAS technique is needle trap microextraction (NTME). More recently, in-tube extraction (ITEX) has been developed and exploited. In addition to these two, miniaturised sorption traps have also been utilised for different air sampling applications.

3.1.1. Needle trap microextraction

NTME as a versatile air sampling technique is applicable for both AAS (introduced in this section) and PAS (introduced in Section 3.2.3). The first needle trap device (NTD) was introduced in 2001 by Pawliszyn's group for particle sampling from air and it acted as a trap for particles rather than for VOCs [25]. It comprised a 23-gauge syringe needle and a bed of quartz wool (5 mm length), which enabled convenient GC injection. The NTD was connected to a syringe that assisted the sampling by a plunger moving up and down. The NTD was thermally desorbed in the GC inlet and the released analytes were flushed by an extra 10 μL of clean air or carrier gas into the GC system. This quartz wool-NTD was used to determine particle-bounded SVOCs and VOCs. This new concept provided great potential for on-site air sampling that is inexpensive, easy to use and robust [24].

In order to analyse free airborne VOCs, in 2005 NTDs packed with sorbent materials were manufactured [26]. Two types of NTD were introduced that concerned the ease of sorbent packing and thermal desorption (TD). The first type of NTD had an opened needle tip and a single bed of sorbent material, after which the opened end was placed at a distance depending on the application (>0 mm and ≥ 0 mm for PAS and AAS, respectively; Figure 1a) [24]. The sorbent was mixed for 5 min with epoxy glue to avoid leakage or spills from the sorbent through the opened end. A gentle air stream continuously passed through the sorbent bed before the glue cured to prevent the needle from blockage. Instead of using glue, a metal wire, metal frit, metal spring, or spiral plug could also be used to stabilise the sorbent bed [24, 27]. A side hole for desorption was drilled above the packing after the sorbent bed. Carrier gas entered the needle from the side hole and flushed the desorbed analytes out from the open end. The second type of NTD had a blunt tip with a small side hole below the packing (Figure 1a). Quartz wool was firstly packed at the front of the needle [26] or the sorbent was mixed with a similar size of glass beads [28] to prevent the blockage of the side hole and to eliminate the memory of analytes which were extracted by the sorbent near the needle tip. An extra syringe filled with clean air or carrier gas was used to flush the desorbed VOCs into the GC column. A similar NTD (NeedlEx) was also introduced by Ishizawa et al. at about the same time and was

used for the analysis of propylene glycol monomethyl ether in soft drinks [29] and light mineral oils [30].

Figure 1.

Due to the limited sorbent mass (normally 1–4 mg) [34], the sampling flow rate should be accurately adjusted before air sampling for quantitative results. The allowed maximum flow rate for different NTDs, either fabricated in the laboratory or commercially available, varied between 1–30 mL min^{-1} due to differences in sorbent material combination, sorbent mass and size, analyte polarity, and analyte concentration [28, 35-37]. Humidity has no significant effect on NTME sampling if the sorbents are properly selected [37, 38] and the variation caused by humidity can be compensated by using an internal standard (ISTD) [39].

3.1.2. In-tube extraction

In-tube extraction (ITEX) is an exhaustive sample preparation technique [40] and was upgraded in 2009 to be compatible with many commercial autosamplers (Figure 1b). The ITEX device is a single piece stainless-steel needle with special shape: an upper part consisting of a larger diameter tube, packed with sorbent material, and a lower part having an ordinary needle cannula with a side hole for septum penetration in the GC inlet. It is connected to a syringe in an ITEX autosampler tool, which consists of an electronic heater and a fan [41, 42]. For ITEX desorption, the syringe aspirates a fixed volume of helium from the GC inlet and the heater simultaneously heats the ITEX rapidly to the desorption temperature (<1 min). The syringe plunger is then moved down to inject the desorbed analytes with a fixed desorption flow rate into the GC. The ITEX system enables an independent desorption temperature from the injector temperature so that pre-conditioning can be processed without occupying the GC inlet. During pre-conditioning, the syringe plunger is lifted over the side hole of the syringe and a continuous flow of nitrogen passes through the packing material from up to down.

Compared to NTME, ITEX features more exhaustive characteristics with larger sorbent volume (~120 μL), which predicts its great potential for air sampling. However, the ITEX has not been considered as a good option for breath air sampling [43]. Recently, the first ITEX air sampling for on-site measurement was achieved by utilizing a drone as the carrier [44]. A fully automated ITEX air sampling system has also been successfully developed [45].

3.1.3. Miniaturised sorption traps

A type of miniaturised sorption trap was introduced in 1993 to enrich VOCs before sensor detection [46]. The trap (3.2 mm, i.d.) was packed with Tenax particles and glass wool. After sampling, the sorption trap was heated by out-wrapped nichrome wire to release the trapped VOCs into a smaller gas volume for sensor analysis. This improved not only the analytical sensitivity but also the baseline stability and humidity resistance [47]. Several miniaturised sorption traps with a smaller size and more functions have also been introduced. A stainless-steel tube and Co-Ni alloy was preferred over a glass tube due to higher mechanical strength (Figure 1c). The dimensions of the metal tube varied from approximately 1.15–5.4 mm (i.d.) × 32–80 mm (L) and the sorbent mass was around 1–20 mg [31, 47-54]. These traps have been packed either in single or segmented beds with

several commercially available sorbent materials, such as carbon molecular sieves (CAR-569, CAR-1000, and Carbosieve SIII) [31, 48, 50-53], graphited carbon (Carbopack and Carbotrap) [31, 48-54], and porous polymers (Tenax and XUS565) [47, 48]. Further, the sorption trap was coupled with an electric circuitry for on-line sampling [31]. Due to many advantages of large-volume sampling (rapid desorption, narrow VOCs plug width, and excellent resistance to saturated humidity), its applications have been extended to trap VOCs from breath air [50-53], perfume vapour [51], essential oil headspace [51], atmospheric air [51, 53], and indoor air [51, 54].

3.2. Miniaturised passive air samplers

MPAS techniques include mainly diffusion-based systems, such as solid-phase microextraction (SPME) in different formats (e.g., fibre, Arrow, and thin film) and solid-phase dynamic extraction (SPDE). An extended diffusion path is used in a retracted SPME fibre and opened end NTD.

3.2.1. SPME fibre

SPME was introduced in the 1990s as a simple, and time and labour saving MPAS technique [55]. Its other advantages include miniaturised sampler size, reusability, and a sensitivity comparable to other traditional PAS techniques. The original SPME has a rod fibre format, where a metal or fused silica fibre has been coated with a small volume (< 1 μL) of absorbent or adsorbent phase (Figure 1d). During air sampling, the SPME coating is directly exposed to the air and VOCs are distributed between the SPME coating and the air. The SPME fibre is then transferred into the GC inlet for thermal desorption. The crucial property of SPME techniques is the ability for quantitation which can be described by equations (1) and (2) [56]. In the case when only two phases (fibre coating and air) exist, the mass of analyte extracted on the SPME fibre can be written as equation (1) based on the law of mass conservation:

$$n = C_f^{\infty} V_f = C_0 \frac{K_{fs} V_s V_f}{K_{fs} V_f + V_s} \quad (1)$$

where n is the mass of analyte that is extracted by the SPME fibre, C_f^{∞} is the equilibrium concentration of analyte in the fibre coating, V_f and V_s are the volumes of the fibre coating and air, respectively, C_0 is the original concentration of analyte in the air, and K_{fs} is the distribution coefficient between the coating and the air. Because air volume $V_s \gg K_{fs} V_f$, equation (1) can be therefore simplified to (2):

$$n = C_f^{\infty} V_f = C_0 K_{fs} V_f \quad (2)$$

Equation (2) exhibits the linear relation between the mass of analyte extracted by the fibre coating and analyte concentration in the air, which demonstrates the quantitativeness of the SPME technique for air sampling.

Because on-site measurements with high time resolution at remote areas have become popular [57, 58], the equilibrium-based SPME fibre sampling approach is impractical. This can be improved by terminating the sampling before equilibrium and enhancing the distribution coefficient between the sorbent phase and the analytes. Dynamic SPME sampling with a fast and known air flow through the fibre can compress the thickness of the boundary layer, thereby resulting in faster sampling [56, 57]. The optimal SPME coating should be carefully selected before air sampling. Several tools, such as an interface model, a cross-flow model, in-fibre standardization calibration, and standard-free calibration, have been developed to quantify concentrations of VOCs in fast-sampled SPME fibres [59]. However, it is still difficult and time-consuming to compare SPME fibre system to other MAAS techniques. Further, the accuracy of the quantitative results should be carefully evaluated [60, 61]. For this reason, only qualitative results are reported [57, 58, 62-65].

In order to meet the diverse requirements for PAS, different SPME configurations, e.g., retracted SPME fibre and thin film microextraction (TFME), have been developed. Retracted SPME fibre was introduced in 1999 as a diffusive sampler for TWA sampling [66]. In contrast to conventional SPME sampling, the TWA sampling was processed by retracting the SPME fibre a known distance (*z*) into its outer needle instead of exposing it outside (Figure 1e). This device met all three prerequisites for successful diffusive PAS: zero sink, short response time, and insensitivity to face velocity. It also demonstrated good resistance to several environmental conditions, e.g., the velocity of air flow that passed the needle tip, temperature, pressure, relative humidity, and ozone. The adjustable diffusion path length in the outer needle makes it more tolerant to changes in analyte concentration and sampling time. The quantitative TWA sampling by retracted SPME fibre is well described by Fick's first law of diffusion (equation 3):

$$n = D\left(\frac{A}{L_d}\right)CT \quad (3)$$

where n is the collected mass of the target analytes, D is the diffusion coefficient of the analytes (cm^2/min), A is the open area of the SPME device, L_d is the diffusive path length (cm), C is the analyte concentration in the air (ng mL^{-1}), and T is the sampling time (min). Since n, A, L_d, and T can be easily measured, and D is found from literature, VOC concentration can be calculated.

The first TFME for VOC analysis used a thin sheet of PDMS membrane as the sampler and it could be rolled around for immediate TD in the GC injector (Figure 1f) [67]. Compared to EVA- and PE-TFME, the PDMS membrane is much smaller and is compatible with commercial TD tubes for further automated desorption and analysis. Particle-based TFME was introduced in 2013 [68] and included DVB particles as the adsorbent for TWA sampling of benzene from outdoor air. The development of TFME devices has mainly been aimed at: 1) faster equilibrium speed, 2) higher sampling capacity, 3) easier handling, and 4) automation.

3.2.2. SPME Arrow

SPME Arrow as an excellent alternative to SPME fibre was introduced by CTC Analytics AG, Switzerland in 2015 [41, 44, 69-72]. It is a completely redesigned and relatively new SPME device which integrates the advantages of the conventional SPME fibre and stir bar sorptive extraction

(SBSE), while excluding their drawbacks. Instead of fused silica or metal fibre, a stainless-steel rod is employed as the coating substrate to prevent physical damage during sampling or GC injection (Figure 1g). In addition, the arrow tip enables SPME Arrow to be closed completely and penetrate the GC inlet gently when withdrawing the rod into the outer stainless-steel needle, thus eliminating contamination during the transfer and/or transportation process and physical damage. In addition, SPME Arrow includes a larger volume of coating (3.8–11.8 µL) with approximately the same coating thickness (100–250 µm) [73] as SPME fibre (0.028–0.612 µL and 7–100 µm) [74], dramatically improving the loading capacity while keeping the fast sampling speed [75]. However, the GC inlet hole needs to be slightly enlarged for SPME Arrow. Commercially available CAR-1000-, PDMS/DVB-, and Carbon wide range (CWR)/PDMS-SPME Arrows have been utilised for the sampling of aliphatic amines [69] and biogenic VOCs, e.g., monoterpenes and aldehydes [75]. In addition, commercial and laboratory-produced SPME Arrows have been successfully loaded onto drones for horizontal and vertical sampling in boreal forest and wetlands [44].

3.2.3. Opened end needle trap device

An NTD with an opened end is feasible for PAS. The basic principle is based on the diffusion of VOCs from air to the NTD tip and then to the packed sorbent materials over a period of time. The VOCs' concentration in air can be calculated by Fick's first law of diffusion following the same principle as with the retracted SPME fibre [26]. In 2014, a new prototype of extended tip NTD was utilised for on-site VOCs measurements [75]. Together with the new NTD, a new deployable pen-like diffusive sampler was built and tested.

3.2.4. Other miniaturised passive air sampling techniques

A few other MPAS techniques have been reported. An SPME-type technique, named solid-phase dynamic extraction (SPDE), has been used for PAS of toluene and biogenic VOCs [77, 78]. It includes a short stainless-steel needle, coated inside with a thin film of stationary phase (Figure 1h). This design increases the volume of stationary phase, leading to a higher analytical sensitivity. In addition, it is more durable which results in a longer coating lifetime compared to conventional SPME fibre. SPDE is a dynamic sampling technique. During sampling the syringe plunger is moved up and down several times to facilitate the equilibrium between VOCs and the sorbent film. After sampling, a certain volume of desorption gas is aspirated before the SPDE device is introduced into the GC inlet for TD. Subsequently, the plunger moves down to flush the desorbed VOCs into the GC system.

SBSE is another alternative system to SPME [73]. A magnetic stirring rod is used as the substrate (Figure 1i). In order to avoid the catalytic effect of the metal on the PDMS layer, the magnetic rod is covered by an extra glass jacket. The typical sorption phase of PDMS has a coating thickness of 0.5–1 mm and volume of 25–125 µL, which is 50–250 times higher than that of PDMS-SPME fibre. Before sampling, the stir bar is loaded into the desorption glass tube and is pre-conditioned in the TDU for a period of time, typically a few hours due to the large volume of PDMS. The TDU can be coupled with a GC autosampler for high-throughput analysis of the sampled stir bars, which are packed in desorption glass tubes. The advantages of SBSE are a high sensitivity and low environmental impact. However, using tweezers to transfer the stir bar between the GC vials, desorption tubes, and sampling spot, is not as convenient as previously mentioned techniques. Up to now, PAS with SBSE has been employed for measuring allethrin and piperonyl butoxide [79].

3.3. Integration of miniaturised passive and active air sampling techniques

Simultaneous sampling by MPAS and MAAS samplers is another attractive approach in air analysis. Equilibrium-based SPME fibre/Arrow and TFME can only enrich free VOCs, whereas the exhaustive NTME and ITEX can collect both free and particulate-bound molecules. Currently, SPME fibre–NTME [25, 80-82], SPME fibre–NTME-TFME [33], and SPME Arrow–ITEX [44] systems have been employed. The information obtained from different sampling techniques provides complementary and comprehensive characterisations of air.

4. Applications

MAS techniques have been widely developed and utilised for sampling VOCs from indoor air, outdoor air, breath air, plant emissions and food [43, 60, 61, 83, 84]. No single MAS technique exists that is suitable for all the applications. The properties of air vary in humidity, temperature, ozone concentration, particle concentration, analyte concentration, etc. In addition, VOCs display a wide range of chemical and physical properties, e.g., polarity, boiling point, molecular size and hydrophobicity. Depending on the desired application, an appropriate MAS technique and configuration should be carefully evaluated before field sampling. Applications of MAS techniques for outdoor, indoor, and breath air sampling are summarised in Tables 1–3. MAS for emissions measurements for solid matrices, e.g., plants and food, are listed in Table 4.

4.1. Outdoor air analysis

The anthropogenic and biogenic VOCs in the troposphere have direct or indirect influence on the physical and mental health of humans. Hence, more MAS applications have focused on measuring toxic VOCs to evaluate and monitor outdoor air quality and air pollution. During recent years, MAS systems for biogenic and reactive VOCs, which can affect our life by changing the Earth's atmosphere or forming toxic products, have gained more attention.

An ideal system for rapid on-site measurement in remote regions is a MAS device coupled with a portable GC-MS, which overcomes problems such as analyte loss, degradation, and contamination during storage and transportation [34]. Some reactive and instable VOCs, e.g., monoterpenes, amines, and acids, do not withstand storage in a carbon-based or DVB adsorbent.

SPME fibre and NTME with portable GC-MS system have been utilised for field measurement of biogenic and anthropogenic VOCs in the atmosphere at the Station for Measuring Ecosystem-Atmosphere Relations II (SMEAR II) in Hyytiälä, Finland [34, 57, 58]. Dynamic SPME fibre sampling (Figure 2a) with portable GC-MS detection allowed fast on-site analysis of monoterpenes, their oxidization products, and amines. The amounts of α-pinene oxidation products and dimethylamine/ethylamine dramatically decreased during the period of the day when nucleation occurred, which indicated the involvements of these VOCs in aerosol formation and growth processes. Owing to the fast air flow around the SPME fibre, the extraction kinetics were accelerated and the influence of wind speed on the SPME fibre sampling was reduced [57]. Due to the ultra-trace concentration of VOCs at the sampling site, SPME fibre was replaced by NTD in order to identify and semi-quantify the most prevalent monoterpenes and aldehydes (Figure 2b) [34]. Besides the biogenic VOCs, anthropogenic ethylbenzene and *p*- and *m*-xylene were also detected when the wind direction was from cities with substantial anthropogenic activities. Accumulation of monoterpenes and aldehydes under or in the snowpack was observed during the autumn campaign. At understory

level, monoterpenes and aldehydes in soil chambers and ambient air were studied with static and dynamic SPME fibre sampling [58]. The most abundant monoterpenes were α-pinene and Δ3-carene, with concentrations similar in soil chambers and ambient air. However, the concentrations of aliphatic aldehydes in ambient air were higher than in soil chambers. A significant contribution of emissions from nearby sawmills was ascertained.

Figure 2.

Using a single MS instead of conventional GC-MS is a feasible way to shorten the total analysis time. NTD coupled with a TD photoionization ToFMS enabled the desorption-detection process to be completed in 10 seconds (Figure 3) [37]. Even though the GC was not used for the separation of analytes, it was still needed for NTD desorption. The desorbed VOCs were transferred to the ion source by a deactivated heated fused silica capillary (250 °C) under helium flow from the GC inlet. This NTME-GC-MS analysis was also implemented to precisely identify the measured VOCs and enhance the selectivity of the MS detector. Further, the NTME-REMPI-ToFMS system was utilised to analyse diesel engine exhaust. Because the study was focused on aromatic substances and PAHs, the ionization wavelength of REMPI-ToFMS needed adjustment [85].

Figure 3.

The applicability of MAS techniques can be further extended by coupling to a high-mobility unmanned drone. The great applicability and potential of drones as a platform for measurement and sampling devices for atmospheric and environmental research at different spatial dimensions has been proven [86-90]. Furthermore, the use of electrically powered engines in the drone minimises potential contamination during sampling, and offers an important alternative to other air sampling platforms, e.g., fixed building/tower, balloons, and aircrafts, due to its excellent flexibility and temporal-spatial capacities [89]. Cheng's group installed a DVB-NTD on a DJI Mavic Pro quadrotor drone to collect toluene, ethylbenzene, and *p*-xylene [91]. Due to air turbulence generated by the propeller rotation influencing the NTME sampling, the NTD position on the drone was designed after simulating flow streams around the propellers by flying the drone through a dry ice spray. A telescope shaft extended the NTD out from the strong downward stream of the propellers. The total mass of the NTD, telescope shaft, Teflon sampling tube, and air-extracting pump was only 200 g, which enabled the light and foldable drone to fly for up to 21 min. This kind of NTME-drone system allowed the collection of VOCs from a pilot VOC exhaust system and it outperformed Teflon sampling bags [92] and stainless-steel canisters [93] for outdoor air sampling.

Drone has also been used as an excellent carrier for simultaneous SPME Arrow and ITEX sampling (Figure 4) [44]. A remote controlled sampling box under the drone enabled SPME Arrow and ITEX sampling to be started and terminated after taking off and before landing the drone, respectively. An extra laboratory-made TDU was utilised for TD of the ITEX device after sampling [94]. Prior to this, the used ITEX was back-flushed by a nitrogen flow for a few seconds to eliminate oxidation during desorption. Later, these SPME Arrow-ITEX-drone and TDU-GC-MS systems were employed for air monitoring at the SMEAR II station (Hyytiälä, Finland). The effects of ITEX accessories (particle, ozone, and water traps), drone horizontal and vertical (5 and 50 m of height) displacements, and sampling site (wetland and forest) on the number and concentration of VOCs were successfully evaluated.

Figure 4.

A fully automated on-line dynamic ITEX-GC/MS system was constructed to integrate the air sampling and measurement steps under full automation. It was used for long-term VOC monitoring in atmospheric air without any human intervention (Figure 5) [45]. The autosampler hardware and software were modified to allow fully automated ITEX movements, including ITEX preconditioning, ISTD addition, dynamic air sampling, and desorption. Instead of plunger up-down strokes, dynamic air sampling allowed a higher sampling flow rate, larger sampling volumes and, consequently, lower detection limits. After sampling, the air flow was closed and desorption gas (helium) was aspirated from the GC inlet and analytes were desorbed and injected into the GC-MS system. Two laboratory-made permeation systems were used for ISTD addition and the calibration of VOCs. A consecutive 19-day atmospheric air measurement campaign under full automation validated the stability and suitability of the developed system. This ITEX-GC/MS method demonstrated exceptional sensitivity, picogram per litre limit of detection (LOD), and great applicability for continuous and quantitative monitoring of VOCs in air.

Figure 5.

Tursumbayeva et al. transformed a fragile SPME fibre into a rugged sampler to lengthen its lifetime in remote locations [95]. The new diffusive sampler used the exposed SPME fibre coating as the sorbent phase and a glass liner as the diffusion path, which facilitated the diffusion of VOCs from air onto the SPME fibre coating (Figure 6). The new device was utilised for field sampling together with sorbent tubes to actively sample in four different locations. The TWA SPME sampling results matched well with the sorbent tube results. They also studied the retracted SPME fibre with different retraction depths (5 and 10 mm) and different materials (CAR/PDMS, PDMS, polyacrylate, and PDMS/DVB) [96, 97]. Retracted SPME fibre was compared with SPME fibre for BTEX sampling from atmospheric air. CAR/PDMS SPME fibre enabled higher analytical sensitivities to benzene and toluene. The retracted SPME fibre extracted two orders of magnitude less mass compared to exposed fibre (with the same material) for BTEX sampling, and shorter storage time was also observed.

Figure 6.

Parshintsev et al. developed an on-fibre derivatization SPME method for atmospheric alkylamines that resulted in increased sensitivity and selectivity [98]. 2,3,4,5,6-Pentafluorobenzyl chloroformate- and 9-fluorenylmethoxycarbonyl chloride-coated PDMS/DVB-SPME fibres were used to sample primary, secondary, and tertiary amines and ammonia quickly and the derivatives could be measured with good time resolution. The LOQ for dimethylamine in selected ion monitoring (SIM) mode was 2.8 ng L^{-1} and atmospheric alkylamines were successfully detected and quantified.

SPME Arrow, TFME, and SBSE have more than 6 times the volume of sorbent compared to SPME fibre and therefore can sample more VOCs under the same sampling time. Commercial PDMS/CAR-1000-, CWR/PDMS-, and PDMS-DVB-SPME Arrows and laboratory-made MCM-TP-SPME Arrow have been employed to collect VOCs from a suburban area of Helsinki and the SMEAR II station [69, 72, 75]. Owing to the large sorbent volume, SPME Arrow gave low LOQs for dimethylamine (33 pg L^{-1}) and trimethylamine (0.43 pg L^{-1}) [69]. Mesoporous silica-coated SPME Arrow provided specific selectivity to alkylamines [72]. Compared to PDMS/DVB-SPME fibres,

SPME Arrow with the same coating material was able to collect over 2 times more monoterpenes and 7–8 times more aldehydes [75]. A DVB/PDMS TFME was reported for air sampling of benzene at a crossroad in the Waterloo region, Canada [68]. Its large surface area (~2.3 cm^2), allowed the equilibrium time to be shortened to 20 min, which is more practical for quantitative and fast VOC monitoring.

Simultaneous use of MAAS and MPAS devices can provide more comprehensive information of air, not only of free VOCs but also of particulate-bound compounds. Li et al. used NTD and SPME fibres to study the gaseous and total VOC concentration in NaCl aerosol, barbecue smoke, and cigarette smoke [99]. The results showed that mainly gaseous analyte molecules were deposited on the fibre coating. The particulate deposit on the fibre coating decreased with increased particle size. NTD can trap both particles and free molecules and the collection efficiency of particles increases with particle diameter (particle diameter should be >0.8 μm).

Table 1. Application of MAS techniques for outdoor air sampling.

MAS technique	Analytes	Sorbent phase	Qualitative /Quantitative	Sampling condition	Desorption condition	LOD/LOQ	Air type	Detection	Reference
NTME	Toluene Ethylbenzene *m*-, *o*-, *p*-Xylene Styrene Phenol 1,2,4-Trimethylbenzene Naphthalene 1-Methylnaphthalene Phenanthrene	PDMS (10 mm) Carbopack B (10 mm) CAR-1000 (10 mm)	Qualitative	10–15 mL	290 °C <10 s		Engine exhaust	PI-ToF-MS	[85]
NTME	13 Anthropogenic and biogenic VOCs	Tenax TA (1 mg) CAR-1016 (1.6 mg) CAR-1003 (1.5 mg)	Qualitative	100 min 25 mL min^{-1}	270 °C 10 s		Atmospheric air	Portable GC-MS	[34]
NTME	Toluene Ethylbenzene *p*-Xylene	DVB (7 mm)	Quantitative	Not mentioned	Temperature not mentioned 30 s	Not mentioned	Atmospheric air	GC-FID	[91]
ITEX	Toluene *p*-Xylene Benzaldehyde Acetophenone 1,2,3-Trimethylbenzene	Polyacrylonitrile (50 mg)	Quantitative	56 mL min^{-1} 30 min 1.68 L	250 °C ~1 min 0.8 mL Helium	25–120 pg L^{-1} (LOQ)	Atmospheric air	GC-MS	[45]
SPME fibre	Benzene	DVB/CAR/PDMS (50/30 μm)	Quantitative	15 min (atmospheric air) 30 s (breath air)	250 °C Time not mentioned	0.24±0.01 ng L^{-1}	Atmospheric air	GC-MS	[100]
SPME fibre	Monoterpenes Amines	PDMS/DVB (65 μm)	Qualitative	2 h (Dynamic sampling, air flow rate 39.7 m^3 h^{-1})	270 °C 10 s		Atmospheric air	Portable GC-MS	[57]
SPME fibre	BTEX	PDMS (100 μm) PDMS/DVB (65 μm) CAR/PDMS (85 μm)	Quantitative	3 min 20 mL	250 °C Time not mentioned	11–57 ng L^{-1}	Atmospheric air	GC-MS	[96]
SPME fibre	BTEX	Cavitand 1 (~35 μm)	Quantitative	15 min 1 L	250 °C 2 min	0.4–1.2 pg L^{-1}	Atmospheric air	GC-MS	[101]
SPME fibre	Monoterpenes Aldehydes	PDMS/DVB (65 μm)	Qualitative	40–60 min	270 °C 10 s		Atmospheric air	Portable GC-MS	[58]
On-fibre derivatization SPME fibre	Ammonia Methylamine Dimethylamine Trimethylamine Ethylamine	PDMS/DVB (65 μm)	Quantitative	5–30 min	250 °C 30 s 180 °C 30 s	170 ng L^{-1} (Dimethylamine)	Atmospheric air Cigarette smoke	GC-MS	[98]
SPME Arrow	Methylamine Dimethylamine Trimethylamine	PDMS/CAR-1000 (100 μm)	Quantitative	30 min	250 °C 40 s	0.43–33 pg L^{-1} (LOQ)	Atmospheric air	GC-MS	[69]
SPME Arrow	Monoterpenes Aldehydes	CWR/PDMS (120 μm) PDMS-DVB (120 μm)	Qualitative	45 min	270 °C 2 min		Atmospheric air	GC-MS	[75]
SPME Arrow	Ethylamine	MCM-41 (~20 μm)	Quantitative	20–30 min	250 °C 1 min	0.01–2 ng mL^{-1}	Atmospheric	GC-MS	[72]

	Diethylamine Triethylamine	MCM-TP (~20 μm)				(MCM-41) 0.03–10 ng mL^{-1} (MCM-TP)	air		
TFME (~2.3 cm^2)	Benzene	PDMS/DVB (105 μm)	Quantitative	1 h	250 °C ~3 min in Gerstel TDU	0.3 ng mL^{-1} (Benzene)	Atmospheric air	GC–MS	[68]
Retracted SPME fibre (Z=5 mm)	BTEX	CAR/PDMS (85 μm)	Quantitative	60 min	250 °C Time not mentioned	1.8–5.2 μg L^{-1}	Engine exhaust	GC-MS	[97]

495

Table 1. Application of MAS techniques for outdoor air sampling (Continued).

MAS technique	Analytes	Sorbent phase	Qualitative /Quantitative	Sampling condition	Desorption condition	LOD/LOQ	Air type	Detection	Reference
Retracted SPME fibre (Z=17 mm)	Acetic acid	Car/PDMS (85 µm)	Quantitative	0.67–12 h	240 °C Time not mentioned	10 ng L^{-1}	Atmospheric air	GC-MS	[95]
SPME fibre NTME	α-Pinene	100 µm PDMS (SPME fibre) 65 µm PDMS/DVB (SPME fibre) 75 µm CAR/PDMS (SPME fibre) 10 mm of DVB (NTD) 10 mm of CAR (NTD)	Quantitative	40 min (SPME fibre) 1.9 mL min^{-1} 50 mL ~25 min (NTD)	300 °C 2 min	Not available	Barbecue cooking Cigarette smoke	GC-MS	[99]
SPME Arrow ITEX	39 VOCs	120 µm PDMS/DVB (SPME Arrow) ~20 µm MCM-Ti (SPME Arrow) 120 µm CWR/PDMS (SPME Arrow) Tenax GR (ITEX) Tenax TA (ITEX) 50 mg of polyacrylonitrile (ITEX)	Qualitative	15–30 min	250 °C 1 min (SPME Arrow) 250 °C 2 min 1.2 mL of Nitrogen (ITEX)		Atmospheric air	GC-MS	[44]

4.2. Indoor air analysis

Indoor air quality is important for the health and comfort of building occupants. Owing to the increasing time that people stay at home and the working environment, the attention to safety aspects has grown in residences. Accordingly, the number of studies describing the evaluation of the air quality in indoor environments has also increased.

Alonso et al. have applied a capillary microtrap TD module for near real-time monitoring of benzene, 2,5-dimethylfuran, toluene, and *m*-, *p*-, and *o*-xylene in indoor air [53]. The simplified design of the microtrap enabled the injection of thermally desorbed VOCs into a GC-FID or GC-MS system without the need for a second cryotrap for focusing. Well-selected and large quantities of sorbent materials, ca. 10.5 mg of weak to strong adsorbent, allowed the detection of VOCs at sub-pptv level.

NTD is also a useful tool for indoor air analysis. Eom et al. constructed two single-bed (DVB or CAR-1000) packed NTDs for BTEX sampling in a chemistry laboratory [102]. Because of the small quantity of adsorbent (<1 mg), the maximum flow rate and sampling volume were only 1.9 mL min^{-1} and 20–150 mL, respectively. This limitation can be overcome by packing a longer sorbent bed [103]. A portable sampling case (34 cm×30 cm×14 cm) is also available to accurately control the flow rate (1–50 mL min^{-1}) [35]. Inoue et al. reported that the maximum flow rate and sampling volume can be 20 mL min^{-1} and 200–800 mL, respectively, by using 25 mm long DVB packing [104]. This device was later applied to determine the VOCs in newly built primary schools in Japan but the concentration levels of VOCs in most of the classrooms were low [104]. In addition to commercial sorbents, laboratory-made graphene nanosheets [105], single wall carbon nanotubes [106], and silica-carbon nanotube composites [107] have been utilised as NTD packing materials. One of the specific aims of these studies was to compare the applicability of these laboratory-made NTDs with commercial NTDs in terms of sampling flow rate, breakthrough volume, storage time,

and sensitivity. Laboratory-made NTDs showed comparable or better performance for sampling of perchloroethylene and volatile organohalogen compounds compared to commercial NTDs.

NTD is also feasible and practical for TWA sampling when using an opened end needle. Gong et al. provided more experimental support for this conclusion [108]. The authors evaluated the effects of temperature, pressure, humidity, and face velocity on the BTEX uptake efficiency of CAR-1000-NTD. The results showed that this NTD behaved like a zero sink for BTEX, its response time was much shorter than the sampling time, and its face velocity does not affect the sampling efficiency, all of which match the prerequisites of a useful diffusive TWA sampler. Furthermore, the abovementioned environmental factors had no obvious effect on CAR-1000-NTD sampling. The applicability of this device for field sampling was proven after constructing two portable CAR-1000-NTD diffusive samplers followed by automated desorption. To ensure more efficient sampling, another extended tip NTD was developed that could be loaded into a holder to form a pen-like diffusive sampler [76] (Figure 7). The loading step was convenient and completed in a few seconds, which was much faster than in previous designs [108]. This new portable sampler was used for TWA sampling of contaminated indoor air and the results were in agreement with those obtained by actively sampled NTD.

The methods that have been reported for the determination of phenol in air are scarce. Es-haghi et al. developed a post on-fibre derivatization SPME method for phenol analysis in occupational air [109]. The retaining time of phenols on the coating was limited; for example, over one third of absorbed/adsorbed phenols were lost after ~2, 8, and 10 min of storage on polar PDMS, PEG 400, and non-polar PDMS coatings, respectively. Therefore, a suitable derivatization reagent was needed to be reversibly loaded onto the fibre after sampling and reacted with phenol to form a well-retaining product. The authors evaluated six types of derivatization reagents and acetic anhydride resulted in the largest derivatization yield and the fastest reaction speed (0.5–1 min), and only produced one stable product. The derivatization conditions should be optimised since the absorbed/adsorbed phenol and the derivatised phenol in the coating can be displaced by excess derivatization reagent or be derivatised at a high temperature.

Figure 7.

A fast and constant air stream passing over SPME fibres can significantly compress the thickness of the boundary layer and, consequently, shorten the equilibrium/sampling time. McKenzie et al. developed a dynamic SPME method as an alternative to the standard surface wipe method for methamphetamine sampling in the field [64]. The dynamic SPME sampler was placed in a fast air flow (1 L min^{-1}) and completed one sampling within the limited access time to the sampling site. In this way, only 5–20 min was needed for sampling, and no sample processing or derivatization was required. Another approach to shorten the sampling time is by decreasing the sampling temperature since the distribution coefficient between the sorbent phase and target compounds can be enhanced at a lower temperature. This was used in the development of a cooled-TFME sampling method (Figure 8) [110]. This approach allowing more sensitive sampling of VOCs was accomplished by decreasing the TFME temperature with a cooling device placed under the TFME system.

Recently, Carter et al. showed a simple SPME fibre method to sample the VOCs above indoor swimming pools [111]. A two-step sampling strategy was utilised, where the air was first collected in

glass vials and then sampled by a DVB/CAR/PDMS-SPME fibre. Storage time clearly influenced the loss of VOCs in the vials, while the effect of storage temperature was not so clear.

Indoor air quality (VOCs) can be more comprehensively characterised by using several different types of samplers at the same time. Eom et al. used SPME fibre, TFME, and NTME simultaneously to sample air from a Cimex lectularius L. infested room [33]. Two important pheromones of bedbugs, (E)-2-hexenal and (E)-2-octenal, were identified by NTME sampling. DVB/CAR/PDMS SPME fibre showed complementary sample fingerprinting and profiling results. The TFME sampling device provided poor extraction for highly volatile and polar VOCs, while its extraction efficiency for less volatile VOCs was excellent. Overall, more than 20 analytes were identified from infested indoor air with the three samplers.

Figure 8.

Profiling the spatial concentration distribution of toxic VOCs in indoor air provides a valuable insight to indoor air quality. Desmet et al. studied the dynamic distribution of pesticide vapours in indoor air by using PDMS-SBSE as a passive sampler [79]. They placed eight stir bars in a contaminated room at two different heights, 1.7 m and 0.9 m, to simulate the breath zone of a person standing and lying in bed, respectively. The SBSE samplers were attached to segmented metal wires by magnetic force and then fixed at the specified heights. Another active PDMS sampler was used to calibrate the SBSE samplers. The spatial concentration profiles of two model compounds showed that the concentration gradient between the source and the corners was present and varied with time.

Controlling the emissions from building materials is a major strategy to reduce concentrations of VOCs in indoor air. Nicolle et al. developed a novel passive sampler, FLEC®-SPME, for passive sampling of VOCs emitted from building materials [112]. FLEC®-SPME is a good alternative to other dynamic sampling protocols aimed at determining the concentration of VOCs in the air at the material surface. This sampler comprised of a standard FLEC emission cell and an SPME fibre. VOCs are first emitted from the material to the cell headspace and then they are retained by the SPME fibre. The first-step equilibrium times for pine wood panel, polyamide carpet, and PVC floor tile were 25, 35, and 65 min, respectively. The SPME fibre sampling time was 20 min. In a 3-day test, the VOCs emitted from these solid materials were identified and quantified. This approach was able to determine 96% of the volatiles specified by the French AFSSET protocol (concentration >5 ng L^{-1}).

Table 2. Application of MAS techniques for indoor air sampling.

MAS technique	Analytes	Sorbent phase	Qualitative/ Quantitative	Sampling condition	Desorption condition	LOD/LOQ	Detection	Reference
Microtrap	Benzene *m*-, *p*-, and *o*-Xylene 2,5-Dimethylfuran Toluene	Carbopack B (5.5±0.2 mg) Carbopack X (2.5±0.2 mg) CAR-1000 (2.5±0.2 mg)	Quantitative	25 min 775 mL 31 mL min^{-1}	0.9 s ~300 °C	16–43 pg L^{-1}	GC-MS GC-FID	[53]
NTME	BTEX	DVB (<1 mg) CAR-1000 (<1 mg)	Quantitative	1.9 mL min^{-1} 5 mL	250 °C 0.5 min (DVB-NTD) 250 °C 1.5 min (CAR-1000-NTD)	Not mentioned	GC-FID GC-MS	[102]
NTME	Toluene Ethylbenzene Xylene Styrene	DVB (25 mm) Activated carbon (5 mm)	Quantitative	20 mL min^{-1} 30 min	250 °C 0.4 mL Nitrogen No preheating time	0.004–0.02 ng L^{-1}	GC–MS	[103]
NTME	Formaldehyde Toluene Ethylbenzene *p*-Dichlorobenzene Xylene Styrene	DVB (25 mm) Activated carbon (5 mm)	Quantitative	50 mL 3 min or 20 mL min^{-1} 30 min	250 °C 0.5 mL Nitrogen No preheating time	<1 ng L^{-1} (50 mL of sampling volume)	GC–MS GC-FID	[104]
NTME	N-nitrosamines	CAR-1000 (10 mm)	Quantitative	4 mL min^{-1} 180–240 mL	265 °C 3 min	1–10 ng L^{-1}	GC-MS	[35]
NTME	Perchloroethylene	Graphene nanoplatelets (15 mm)	Qualitative	3 mL min^{-1} 30 mL	300 °C 3 min	0.023 ng L^{-1}	GC-MS	[105]
ITEX	48 VOCs	Polyacrylonitrile (50 mg)	Quantitative	200 mL min^{-1} 90 min 18 L	250 °C ~1 min 0.8 mL Helium		GC-MS	[45]
NTME (PAS)	BTEX	CAR-1000 (~0.6 mg)	Quantitative	8–40 h	300 °C Time not mentioned	0.60-0.78 ng	GC-MS	[108]
NTME (PAS)	18 VOCs	PDMS DVB CAR	Quantitative	8 h	Not available	Not mentioned	GC-MS GC-FID	[76]
SPME fibre	Phenol	PDMS (10 µm)	Quantitative	5 min	250 °C 3 min	5 ng L^{-1}	GC-MS	[119]
SPME fibre	Methamphetamine	PDMS (100 µm) CAR/PDMS (75 µm)	Qualitative	5–30 min 1 L min^{-1} (Dynamic sampling)	250 °C 1.5 min		GC–MS	[64]
SPME fibre	Trichloromethane Bromodichloromethane Dibromochloromethane Tribromomethane	DVB/CAR/PDMS (50/30 µm)	Quantitative	15 min 20 mL	190 °C 10 min	0.7–2.6 ng L^{-3}	GC-MS	[112]
SBSE	Allethrin and piperonyl butoxide	PDMS (0.5 mm thick)	Qualitative	60 min	300 °C ~6 min in Gerstel TDU		GC-MS	[79]
Cold TFME (1.13–4.91 cm^2)	Limonene Cinnamaldehyde 2-Pentadecanone	PDMS (102 µm)	Quantitative	3 h	Gerstel TDU 250 °C ~4 min	0.1–9.2 ng L^{-1} (Limonene, 30 min sampling)	GC-MS	[110]
SPME fibre NTME	Perchloroethylene	50 µm of Carbon nanotubes (SPME fibre) 15 mm of Carbon nanotubes (NTD)	Quantitative	Not mentioned	250 °C 1 min (SPME fibre) 300 °C 4 min (NTD)	23 ng L^{-1} (SPME fibre) 11 ng L^{-1} (NTD)	GC-MS	[107]
SPME fibre TFME (5 cm^2) NTME	>20 VOCs	50/30 µm DVB/CAR/PDMS (SPME fibre) 126 µm PDMS (TFME) 10 mm of DVB (NTD)	Qualitative	2 h (SPME fibre and TFME) 20 min 5 mL min^{-1} (NTD)	250 °C 1 min (SPME fibre) 250 °C 0.5 min (NTD) 280 °C 5 min in Gerstel TDU (TFME)		GC-MS	[33]
SPME fibre	36 VOCs	CAR/PDMS (75 µm)	Quantitative	25–65 min	320 °C 4 min	0.6–16 ng L^{-1}	GC-FID GC-MS	[112]

4.3. Breath air analysis

Analysis of exhaled air from humans and animals is showing promise for use in early disease diagnosis either by targeted analysis of specific VOCs relating to a disease or by non-targeted analysis to obtain a total profile of volatile metabolites. The challenges for breath air sampling include high humidity, complexity, the existence of exogenous and endogenous substances, and

problems caused by inspired and dead space air. Therefore, more parameters should be considered and optimised before point-of-care applications.

Sanchez et al. have developed several types of multibed sorption traps for human breath air analysis [31, 50-52]. The traps include a Ni-Co alloy (8 cm L, 1.35 mm i.d.) and three or four discreet adsorbent beds containing Carbopack B, Carbopack X, Carbopack Y or CAR-1000 [50, 52]. About 10 mg of total materials are used to ensure sufficient amount of adsorbent to prevent breakthrough even at sampling volumes and sampling flow rates up to 560–800 mL and 40–80 mL min^{-1}, respectively. The authors pointed out that although the carbon molecular sieve adsorbed substantial amounts of water, it is the material of choice when sampling very volatile compounds because of its high adsorption capacity for these compounds. For breath air sampling, the trap was connected to an electronic circuit, valves, and vacuum pump to form an on-line sampling system that enabled the fast and accurate collection of VOCs from breath. For injection of analytes, helium flow (reverse to the sampling flow) in the trap and rapid heating to 300 °C in 1.5 s were used. A 10 s heating pulse was enough to remove the adsorbed VOCs without any carryover. In addition, the on-line operation system reduced the risk of analyte decomposition before desorption or during injection. The analysis was carried out using GC-FID [50] and GC×GC-ToF-MS [52]. The sorption-trap-GC-FID method allowed identification of 25 compounds from the breath air of a smoker, non-smoker, and gum chewer. By using the more powerful GC×GC-ToF-MS, approximately 250 compounds were observed, of which 142 were identified.

Trefz et al. systematically studied the possibility of using NeedlEx NTDs as breath air samplers [37, 113]. NTDs were packed with different combinations of PDMS, DVB, Carbopack X, and CAR-1000 or with a single layer of polymeric methacrylic acid and ethylene glycol dimethacrylate. Polymer-NTD had the most universal VOC coverage, best repeatability and reproducibility, and least carryover (Figure 9) [113]. However, it was not suitable for air sampling of very volatile organic compounds, VVOCs, (< C6) from breath air due to the hydrophilic polymer surface that can be occupied by water [37]. In addition, its maximum flow rate and sampling volume were restricted to 10 mL min^{-1} and 10 mL, respectively. DVB/Carbopack X/CAR-1000 and other multi-bed NTDs were more efficient for high-humid air sampling and water vapour enhanced the desorption efficiency. Specifically, DVB-NTD allowed flow rates of up to 25 mL min^{-1} and sampling volumes to 60 mL. Significant carryover of highly polar VOCs was a general problem in NTDs containing graphitised carbon black but could be circumvented by using a triple sorbent bed instead of a double. DVB/CAR-1000 and DVB/Carbopack X/CAR-1000 packed NTDs were more efficient for aromatic VOCs, while PDMS/Carbopack X/CAR-1000 NTD was a good alternative for the analysis of hydrocarbons and aldehydes if the analytical sensitivity was not an issue. Overall, NTME can achieve LODs and LOQs in the range of ng L^{-1} with 20 mL of air and the sensitivity can be further improved by increasing the sample volume. NTME samplers have great potential for direct alveolar sampling at point-of-care when coupled with an automated CO_2-controlled sampling device consisting of fast responding electronics, valves, and controllers, which can recognise the inspiratory and respiratory cycles [37]. The respiratory cycle was recognised when the CO_2 concentration exceeded a pre-set threshold value in the system, which triggered the sampling valve to open and the vacuum pump to start sucking the breath air through the NTD. During the inspiratory cycle, the CO_2 concentration dropped, and the valve closed. This NTME system enabled automated intermittent

sampling at a rate of 10-12 cycles/min and guaranteed a well-controlled sampling flow, volume, and pressure.

Figure 9.

The NTME technique can be coupled with a GC-autosampler, e.g., by PAS Concept, to achieve automated breath air sampling from sample vials [114] and subsequent automated analysis by GC-MS [27, 108 115, 116]. The magnetic arm transferred the NTD to the GC inlet and the carrier gas flow passed through the Luer-lock adaptor to the NTD and thereby directed the desorbed analytes into the GC column. A cryogenic refocusing trap was needed to avoid any analyte losses due to the programmed GC inlet temperature. In addition to GC-MS detection, Kleeblatt et al. used photoionization ToF-MS to detect the sampled VOCs from breath air [36]. Single photon ionization (118 nm) and REMPI (266 nm) were able to soft ionise the more volatile VOCs and less volatile VOCs, respectively. This approach only needed 10 mL of air sample and enabled sensitive detection of VOCs in the mid- to lower-ppb range and performed well for the analysis of breath air of healthy non-smoking, healthy smoking, and animal subjects, and showed great potential for quantitative on-line NTME-MS measurements.

During breath air sampling, water vapour collected into the active samplers, either retained by the sorbent or condensed on needle walls, has a significant impact on the analytical results, e.g., on repeatability, detection limits, and desorption efficiency. Addition of an ISTD prior to sampling is a useful way to minimise this issue but has been less studied with MAAS techniques. Mieth et al. spiked two sampling cycles of 2,3-dimethyl-1,3-butadiene (35 nmol L^{-1} in Tedlar bag) into the NTD before breath air sampling [115], which helped to prolong the storage in NTD and monitor the desorption system leakage. Strating et al. simply used ethylbenzene as the ISTD for methylene chloride, benzene, toluene, and tetrachloroethylene [117]. Biagini et al. utilised labelled ^{6}D-acetone and ^{8}D-toluene as ISTDs to improve the triple-bed NTD performance at 10% relative humidity, resulting in only 10-20% recovery of VVOCs due to incomplete desorption [39]. Further, the variations in VOC recovery at different humidity levels and storage times decreased to 20% and 10-20%, respectively. Ueta et al. have also used 25 ng of gaseous ^{8}D-toluene as the ISTD [103].

SPME fibre is the most widely employed MPAS sampler for breath air analysis and can be less affected by saturated humidity when using a hydrophobic fibre coating, e.g., a PDMS-contained sorbent phase. Menezes et al. compared benzene concentration in the breath air of two groups of volunteers [100]. They found the benzene content in the exhaled air correlated to the working atmosphere of volunteers. Ma et al. combined PDMS- and PDMS/DVB-SPME fibres with flow-modulated GC×GC-FID to determine lung cancer markers by profiling the breath volatiles of lung cancer patients and healthy volunteers [118]. Acetone, isoprene, methanol, pentane, and propanol were quantified and identified as potential biomarkers of lung cancer due to their exceptionally high concentrations in patients compared to healthy controls. Lu et al. constructed a glassware device to replace the frequently used Tedlar bag for SPME fibre sampling in order to eliminate phenol and N,N-dimethylacetamide contamination [63]. The glass container showed superior cleanness and airtightness even after three days of storage. This approach was used to compare the breath air of Myrtol users and controls and the results indicated that 2,3-dehydro-1,8-cineole is the metabolite of 1,8-cineole, which is a component of Myrtol. New coating materials, e.g., multi-walled carbon

nanotubes [119] and MOFs [120], have been developed to improve SPME fibre selectivity. Yu et al. fabricated a gate-opening controlled zeolitic imidazolate framework (ZIF)-7 coating via a sol-gel

Table 3. Application of MAS techniques for breath air sampling.

MAS technique	Analytes	Sorbent phase	Qualitative/ Quantitative	Sampling condition	Desorption condition	LOD/LOQ	Detection instrument	Reference
Sorption trap	25 VOCs	Carbopack B (2.2–2.5 mg) Carbopack X (2.2–2.5 mg) Carbopack Y (2.2–2.5 mg) CAR-1000 (2.2–2.5 mg)	Quantitative	10 min 800 mL 80 mL^{-1}	300 °C 10 s	1–5 ng mL^{-1}	GC-FID	[50]
Sorption trap	>100 VOCs	Carbopack B (5.5±0.1 mg) Carbopack X (2.5±0.1 mg) CAR-1000 (2.5±0.1 mg)	Quantitative	14 min 560 mL 40 mL min^{-1}	300 °C 10 s		GC×GC-ToF-MS	[52]
NTME	Isoprene Dimethyl sulphide 2-Butenal Hexane Pentane Hexanal Pentanal Acetone	CAR-1000 (1 cm) Carbopack X (1 cm) Tenax (1 cm)	Quantitative	25 s 25 mL 60 mL min^{-1}	300 °C 0.5 min	0.4–8.3 ng L^{-1}	GC-MS	[114]
NTME	61 VOCs	Carbopack X (20 mm) CAR-1000 (10 mm)	Qualitative	5 mL min^{-1} 150 mL	300 °C 1.5 min	Not available	GC-MS	[116]
NTME	>60 VOCs	CAR-1000 (1 cm) Carbopack X (1 cm) Tenax (1 cm)	Quantitative	20 mL ~2 min	300 °C 20 s	0.01–2.51 nmol L^{-1}	GC-MS GC×GC-ToF-MS	[115]
NTME	24 VOCs	Carbopack X (10 mm) CAR-1000 (10 mm) DVB (10 mm) Polymer (20 mm)	Qualitative	15–25 mL min^{-1} 20 mL	250 °C 0.5 min (DVB/Carbopack X/CAR-1000-NTD) 200 °C 0.5 min (Polymer-NTD)		GC-MS	[37]
NTME	Benzene Toluene 1,2,4-Trimethylbenzene Propofol	PDMS (10 mm) Carbopack B (10 mm) CAR-1000 (10 mm)	Quantitative	30 mL 2–3 min 25–30 mL min^{-1}	290 °C <10 s	10.3–30.3 ppb	PI-ToF-MS	[36]
ITEX	Breath biomarkers	Polyacrylonitrile (50 mg)	Qualitative	200 mL min^{-1} 10 min 2 L	250 °C ~1 min 0.8 mL Helium		GC-MS	[45]
SPME fibre	Benzene	DVB/CAR/PDMS (50/30 µm)	Quantitative	15 min (atmospheric air) 30 s (breath air)	250 °C Time not mentioned	0.24±0.01 ng L^{-1}	GC-MS	[100]
SPME fibre	Isoprene Propanol Acetone Pentane Methanol	PDMS (100 µm) PDMS/DVB (65 µm)	Quantitative	10 min	250 °C 3 min	10–100 ng L^{-1}	GC×GC-FID	[118]
SPME fibre	Decane Undecane Dodecane Tridecane Tetradecane	Multi-walled carbon nanotubes (67 µm)	Quantitative	40 min	270 °C 10 min	1–6 ppt$_v$	GC-MS	[119]
SPME fibre	α-pinene, 2,3-Dehydro-1,8-cineole, d-Limonene 1,8-Cineole	CAR/PDMS (75 µm)	Qualitative	60 min	200 °C 30 s		GC-MS	[63]
SPME fibre	Hexanal Heptanal Octanal Nonanal Decanal	ZIF-7 (~30 µm)	Quantitative	15 min	250 °C 2 min	0.61–0.84 µg L^{-1}	GC-FID	[120]

method [120]. The coating thickness was only approximately 30 µm but exhibited excellent extraction capacity and selectivity to aldehydes due to its unique properties, including its specific

porous structure, hydrophobicity, gate-opening effect, and unsaturated metal-coordination sites. The opening window size of ZIF-7 facilitated its accessibility to the target analytes while excluding the relatively large molecular analytes. A multi-walled carbon nanotube-SPME fibre was reported by Tang et al. to selectively sample alkanes from breath of 10 healthy subjects [119]. Trace levels of dodecane and tetradecane were found in all breath samples. These two compounds belong to the 50 most frequently occurring VOCs with negative alveolar gradients. With negative alveolar gradients, decane and undecane are easiest to detect.

4.4. Sampling of VOCs emitted by plants and food

Analysis of the VOCs emitted by plants helps to understand their influential role in interacting with other plants, insects, microbes, and the atmosphere. Bouvier-Brown et al. used SPME fibre to collect highly reactive semivolatile sesquiterpenes, oxygenated terpenes, and methyl chavicol from Ponderosa pine, manzanita, and ceanothus [121, 122]. Plant branches were enclosed in a polytetrafluoroethylene (PTFE) chamber and a zero air (with ambient CO_2 concentration) flowed through the chamber to eliminate contamination by ambient air. The authors demonstrated the suitability of SPME sampling in the chamber enclosed with a Ponderosa pine branch [121]. The same sampler and chamber were used in a 3-month campaign at the Blodgett forest Ameriflux site, California, USA [122]. All the VOCs selected for the study were quantified and the results proved that sesquiterpene and methyl chavicol emissions are crucial contributors to the overall flux of terpenes and methyl chavicol at the sampling site. More methyl chavicol and total sesquiterpenes were measured than previously. In addition, because these VOCs are very reactive with ozone, they affect the chemical ozone flux and form oxidation products. Based on these results, the authors recommended that sequiterpenes and methyl chavicol must be included in biogenic emission models as inputs to SOA models and atmospheric chemistry.

Stierlin et al. have applied a DVB/CAR/PDMS-SPME fibre to sampling the root-emitted VOCs of lavenders and lavandin to evaluate a metabolomic approach to distinguish lavender and lavandin varieties [123]. In total, 99 VOCs, including 40 monoterpenes, 15 sesquiterpenoids, 1 diterpenoid, and 2 coumarins, were detected from four types of lavenders and lavandins. Among them, 15 volatiles were regarded as potential discriminatory compounds and β-phellandrene allowed discrimination between lavender and lavandin species.

Beck et al. [124] used a NTME-portable GC-MS system to collect and analyse the VOCs that are emitted from damaged and undamaged yellow starthistle flower heads in situ. A triple-bed NTD (1.6 mg of Tenax TA, 1.6 mg of CAR-1016, and 1.5 mg CAR-1003) was used to collect the volatiles at a flow rate of 20 mL min^{-1} for 15 min and a Tridion-9 portable GC-MS was used to detect volatiles in a <3 min program. Principal component analysis and analysis of variance were used for statistical analysis. The former analysis distinguished the treatments and identified volatiles, and the latter analysis determined the differences between the amounts of volatiles in different treatments. In total, 31 VOCs were detected from four flow head treatments. Among them, 1-pentadecene, tetradecane, sesquiterpene, cyclosativene and copaene were identified as probable biomarker volatiles for damaged flower heads.

Because of the advantages of portable analytical instruments in field analysis, Reyes-Garcés et al. proposed an NTME/SPME fibre portable GC-ion mobility spectrometry (NTME-GC-IMS)

system specifically for on-site measurements of acetone, limonene, and α-pinene [81]. The advantages of using IMS include low power requirements, small size, and low cost. Disadvantages, such as competitive ionization reactions, narrow dynamic ranges at high concentrations, and limited detectable substances, were addressed by coupling with a miniaturised GC. The field measurement was carried out using SPME and NTME sequentially to collect the volatiles emitted by pine branches. Sampling started 20 min after enclosing the pine branch in a glass sampling chamber. Sampling time and sampling volume of SPME fibre and NTD were 10 s and 1–10 mL, respectively. In the same sampling day, the concentration profiles of α-pinene obtained by SPME and NTME samplers showed a similar concentration trend, while the concentration obtained by NTD was higher than that obtained by SPME fibre, possibly caused by the presence of particulate matter in the sampling chamber. Chen et al. used a similar strategy for in situ monitoring of the emission patterns of VOCs from Calocedrus macrolepis var. formosana Florin leaves [65]. The plant leaves were sealed in a glass chamber. The SPME fibre sampling was performed for 15 min every hour for continuous periods of over 24 h on sunny and rainy days. The emission patterns of three major constituents, α-pinene, limonene, and myrcene, showed three maximum emission cycles in both sunny and rainy weather. One of the peak emissions was seen at around noon and the other two peaks at midnight, which were caused by the plant's circadian clock.

Recently, Rice and co-workers proposed a novel concept for sampling grape-emitted VOCs [62, 125]. They used SPME fibre for non-destructive VOCs from a cold-hardy grape variety in the upper Midwest area of the US. The sampling objectives included the whole grape cluster and single grapes (Figure 10). The whole grape cluster was temporarily enclosed in a polyvinyl fluoride film bag to concentrate the emitted VOCs, and a PTFE port was modified on the bag so that the SPME fibre could penetrate the septum for sampling. For a single grape berry, a 2 mL glass vial was modified by removing flat bottom and the edges were flared and rounded. During sampling, the SPME fibre was supported by a half hole septum, which was screwed at the top of the glass vial. The fibre and vial apparatus were then placed on the single grape berry and a vacuum was formed inside the vial by using a syringe to pull out the air. The SPME fibre was thus exposed above the grape berry and processed the vacuum-assisted sampling. In total, 44 and 39 VOCs were detected from whole grape clusters and single grape berries, respectively, and the concept showed feasibility for detecting VOCs emitted in vivo. In addition, all four cultivars with different temporal and vineyard locations gave varied VOC profiles.

Figure 10.

VOCs are a group of important components in the perception of food flavour. Leinen et al. developed 2019 an SPME sampling method to profile the VOC constituents (aldehydes, alcohols, esters, ketones, organic acids, and terpenoids) of 31 homemade preserved foods prepared during the years 1950–1953 [126]. A 100 μm PDMS-SPME fibre was used to collect the volatiles for 2 h. Surprisingly, bisphenol-A (BPA) was also detected in the concentration range of 3.4–19.2 ng g^{-1} in 29 food jars, indicating these jars belong to the earliest BPA-containing products in the US. At the same time, Ueta et al. also used a MAS device for food emission sampling [127]. An NTD packed with non-volatile carboxylic acid-coated macroporous terephthalic acid particles was used as the active sampler to trap aliphatic amines emitted from raw fish and raw meat. Owing to the exceptional affinity between the sorbent and amines, this approach was able to determine trace levels of amines

783 from food emissions. Amines emitted by the raw meat and raw fish increased with longer storage
784 time due to bacterial growth and spoilage.
785

Table 4. Application of MAS techniques for sampling of VOCs from plants and food emissions.

MAS technique	Analytes	Sorbent phase	Qualitative/Quantitative	Sampling condition	Desorption condition	LOD/LOQ	Air type	Detection instrument	Reference
NTME	Ammonia, Methylamine Dimethylamine Ethylamine Trimethylamine	Carboxylic acid coated macroporous terephthalic acid particles (25 mm)	Quantitative	10–100 mL	240 °C 3 s 0.3 mL of Nitrogen	30–1000 ng L^{-1}	Emissions of raw fish and raw meat	GC-BID	[127]
NTME	31 VOCs	Tenax TA (1mg) CAR-1016 (1.6mg) CAR-1003 (1.5mg)	Qualitative	20 mL min^{-1} 15 min	270 °C 10 s		Emissions of flower head	Portable GC-MS	[124]
SPME fibre	69 VOCs	PDMS/DVB (65 µm)	Qualitative	15 min	250 °C Time not mentioned		Emissions of plant leaves	GC-FID GC-MS	[65]
SPME fibre	Sesquiterpene Oxygenated terpene	PDMS/DVB (65 µm)	Quantitative	10–45 min	200 °C 5 min	4.36–16.6 ng L^{-1}	Emissions of plant branch	GC-MS	[121]
SPME fibre	Sesquiterpenes Methyl chavicol	PDMS/DVB (65 µm)	Quantitative	10–45 min	200 °C 5 min	4.36–16.6 ng L^{-1}	Emissions of plant branch	GC-FID GC-MS	[122]
SPME fibre	67 VOCs (Identified) Bisphenol-A (Quantified)	PDMS (100 µm)	Quantitative	2 h	250 °C 30 min	Bisphenol-A: 1 ng g^{-1} (LOQ)	Emissions of preserved foods	GC-MS	[126]
SPME fibre	>120 VOCs	PDMS/DVB (65 µm)	Qualitative	30 min	250 °C Time not mentioned		Emissions of grapes	GC-MS	[62] [125]
SPME fibre	99 VOCs	DVB/CAR/PDMS (50/30 µm)	Qualitative	60 min	250 °C 4 min		Emissions of plant roots	GC-MS	[123]
SPME fibre	Monoterpenes Aldehydes	PDMS/DVB (65 µm)	Qualitative	40–60 min	270 °C 10 s		Emissions of vegetation	Portable GC-MS	
SPME fibre NTME	α-Pinene Limonene Acetone	65 µm PDMS/DVB (SPME fibre) 10 mm of CAR-1000 10 mm of DVB (NTD)	Quantitative	10 s (SPME fibre) 2 mL min^{-1} 10 mL (NTD)	255 °C 2 min 0.2 mL of Nitrogen	0.037–0.2 ng (NTD)	Emissions of pine branch	Portable GC-IMS	[58]

5. Conclusions and future prospects

MAS techniques, which use miniaturised samplers and configurations, have been introduced to overcome problems related to conventional air sampling techniques, such as their bulk size, long sampling times, high cost, and serious artefacts. MAS techniques simplify the sampling steps and can be fully automated. In addition, they can be integrated with analytical instruments for on-line analysis, resulting in reductions in analysis time, errors, and labour costs. NTME, ITEX, sorption trap, SPME, TFME, SBSE, and SPDE have been widely applied for air sampling prior to gas chromatographic analysis of atmospheric air, indoor air, breath air, and emissions of plants and food. No single MAS technique can meet all the requirements imposed for the analysis of different air types and VOCs with diverse chemical and physical properties. Moreover, different sampling times are often required. The advantages and disadvantages of the reviewed MAS techniques are summarised in Table 5 to simplify selection of the most suitable MAS technique before field sampling.

For screening of VOCs in the air, techniques using miniaturised active air samplers are more suitable than those using miniaturised passive air samplers due to their exhaustive extraction, which allow quantitative trapping of VOCs. With the correct flow rate and sampling time, active samplers can collect sufficient samples for identification and quantitation. However, the choice of the most selective sorbent/coating material and evaluation of the effect of atmospheric conditions (humidity, temperature, wind speed, and ozone) are essential steps before air sampling. Because the evaluation

processes are mainly carried out in the laboratory, the laboratory-designed sampling conditions should resemble as closely as possible the conditions in the field. In this way, sampling and detection errors, and the sampling time can be reduced. Automated MAS systems, e.g., ITEX and SPME fibre/Arrow, are useful for near real-time monitoring of VOCs in air. A fast or portable GC-MS system can then further improve the time resolution. If quantitative results are needed, MAAS techniques are more reliable than others, but comprehensive optimization is still needed to eliminate breakthrough. For TWA sampling, an electronic-free passive sampler is the best option and it can stay at the sampling site from minutes to months. Coupling of active and passive samplers for simultaneous sampling can result in more comprehensive information of the air composition. The miniaturised size of air samplers allows their applicability on different sampling platforms, such as drones, balloons, or aircraft, thus helping to get information on VOCs from more spatial dimensions.

Further developments are still needed to overcome the general drawbacks of MAS techniques, such as the small bed volume of AAS devices which result in a small sample volume and thereby weaker analytical sensitivity compared to conventional AAS techniques. PAS techniques are still difficult for quantitation since they are sensitive to tremendous atmospheric conditions, e.g., humidity, temperature, and wind speed. Furthermore, miniaturised devices require more attention for device fabrication in order to have a reproducibility comparable to conventional AS devices. The PAS devices are still fragile, which needs to be improved in order to obtain more repeatable and reproducible results and improve costs for a single analysis. In addition, an inter-laboratory study would give important information about the reliability and accuracy of a particular MAS technique. The comparability of results between different sampling events by using the same MAS technique has not been studied and reported. Further, official standard air sampling and analysis methods based on MAS techniques and configurations are still missing.

Table 5. Comparison of miniaturised air sampling techniques.

	NTME	ITEX	Sorption trap	SPME fibre	SPME Arrow	Retracted SPME fibre	TFME	SPDE	SBSE
Type of sampler	Active/Passive	Active	Active	Passive	Passive	Passive	Passive	Passive	Passive
Phase volume	~1– ~4 mg	~120 µL	~10 mg	0.026–0.612 µL	3.8–11.8 µL	0.026–0.612 µL	~40– ~100 µL[a]	4 µL	24–126 µL
Typical sampling volume (L)	≤2.5	<18	<0.8						
Typical sampling flow rate	~2–60 mL min^{-1}	56–200 mL min^{-1}	≤100 mL min^{-1}					3 mL min^{-1}	
Fully automated sampling	Yes	Yes	Yes	Yes	Yes	No	No	Yes	No
Manual sampling	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
On-site sampling	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Compatible with portable GC-MS	Yes	No	No	Yes	Yes	Yes	Yes	Yes	No
Quantitativeness	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Quantitation	Easy	Easy	Easy	Difficult	Difficult	Difficult	Difficult	Difficult	Difficult
Carry-over effect	Small	Small	Small	Small	Small	Small	Medium	Small	Medium

[a] Estimated from the data provided by ref. [68] and ref. [110].

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Figure captions

Figure 1. Schematic presentation of miniaturised air sampling techniques, (a) needle trap microextraction (NTME), (b) in-tube extraction (ITEX), (c) sorption trap [31], (d) solid-phase microextraction (SPME) fibre, (e) retracted SPME fibre [32], (f) thin-film microextraction (TFME) [33], (g) SPME Arrow, (h) solid-phase dynamic extraction (SPDE), and (i) stir bar sorptive extraction (SBSE). Adapted with permissions from Refs. [31, 32, 33].

Figure 2. Employment of dynamic sampling techniques, (a) SPME [57] and (b) NTD [34], for monitoring biogenic volatile organic compounds in atmospheric air. E. = a day when a nucleation event was observed, U. = an undefined event and N.E. = a day without nucleation event. Adapted from Ref. [34] under Creative Commons Attribution 4.0 License, and with permission from Ref. [57].

Figure 3. Measurement setup of the NTME-REMPI-ToFMS system. NTD was thermally desorbed in the GC inlet (left side) and the desorbed VOCs were directly transferred to an ion source of REMPI-ToFMS for detection [85]. NTD, needle trap device; GC, gas chromatography; SHG, second-harmonic generation; VUV, vacuum-ultraviolet; HV, high voltage; MCP, multichannel plate; OPO, optical parametric oscillator; SPI, single photon ionization. Adapted with permission from Ref. [85].

Figure 4. Drone as the carrier of SPME Arrow and ITEX for atmospheric air sampling. (a) Front schematic view and detailed pictures showing on/off valves, drone box and a sampling pump, and (b) side schematic view and detailed pictures of SPME Arrow and ITEX connections [44]. Adapted from Ref. [44] under Creative Commons Attribution 4.0 License.

Figure 5. Schematic of the fully automated on-line dynamic ITEX system comprising three steps: (1) preconditioning, (2) ISTD extraction, and (3) standard sampling. The system was employed for (a) on-line dynamic ITEX calibration and method development and (b) air sampling [45]. Adapted from Ref. [45] under Creative Commons Attribution 4.0 License. Further permissions related to the material excerpted should be directed to the ACS.

Figure 6. TWA gas sampling with retracted SPME fibres. (A) Sampling with SPME fibre exposed and retracted inside a glass liner; (B) conventional TWA SPME sampler where SPME fibre is retracted inside a conventional SPME needle; (C) field air sampling by the TWA SPME sampler [95]. Adapted from Ref. [95] under Creative Commons Attribution 4.0 License.

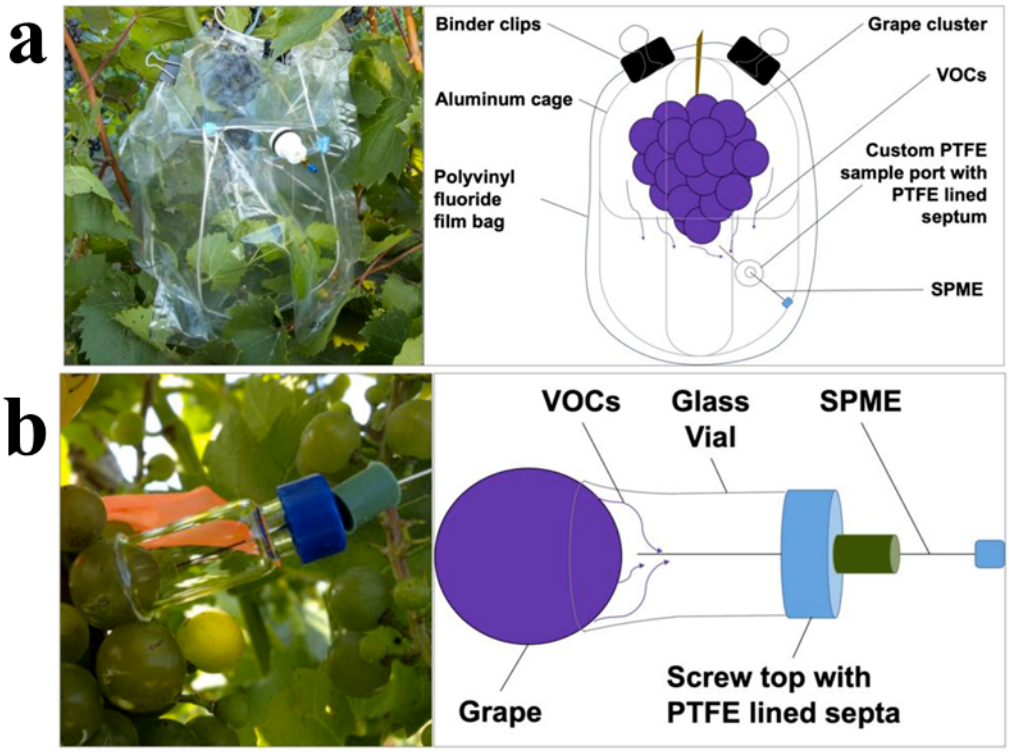
Figure 7. Schematic of the sampling and sealed positions of the pen-like NTME sampler [76]. Adapted with permission from Ref. [76].

Figure 8. Comparison of extraction efficiency with cooling and without cooling for real sample analysis using the cooled membrane device. Sampling time, 3 h. (1) trichloroethylene; (2) toluene;

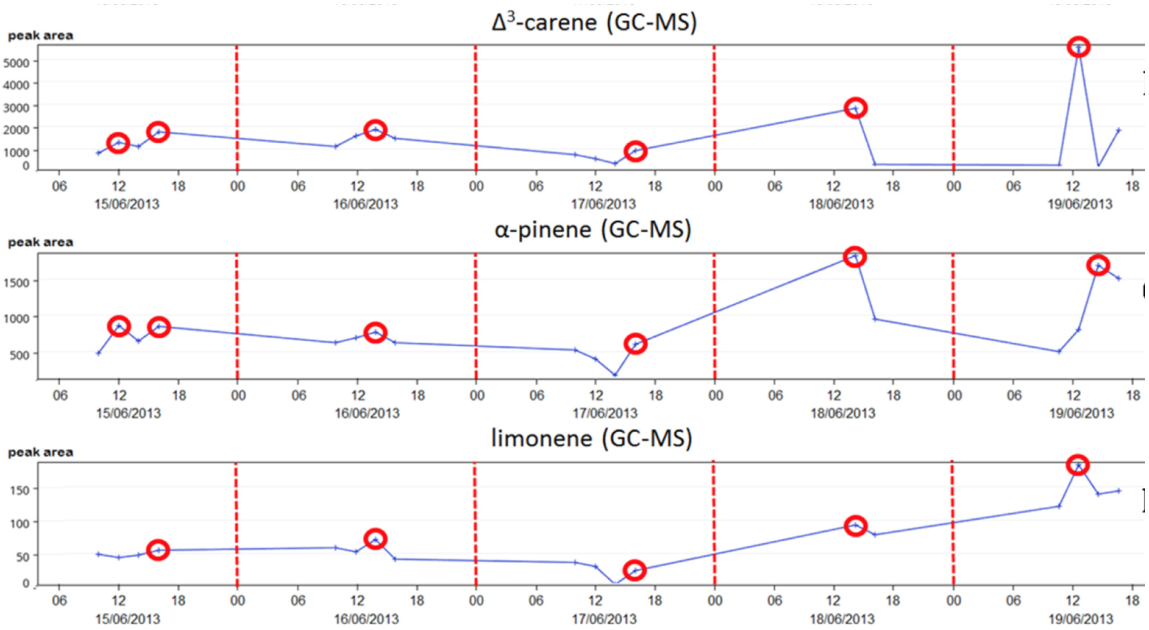
(3) *o*-xylene; (4) nonane; (5) decane; (6) limonene; (7) undecane; (8) nonanal; (9) decanal; (10) undecanal [110]. Adapted with permission from Ref. [110].

Figure 9. Total ion chromatograms from carry over measurements using a polymer-packed NTD (two subsequent 30 s desorption at 200^{o}C) for standard VOC mixture [113]. Blue trace: first desorption; red trace: second desorption. The insert gives a more detailed view (4 -10 min) of the chromatograms. Adapted with permission from Ref. [113].

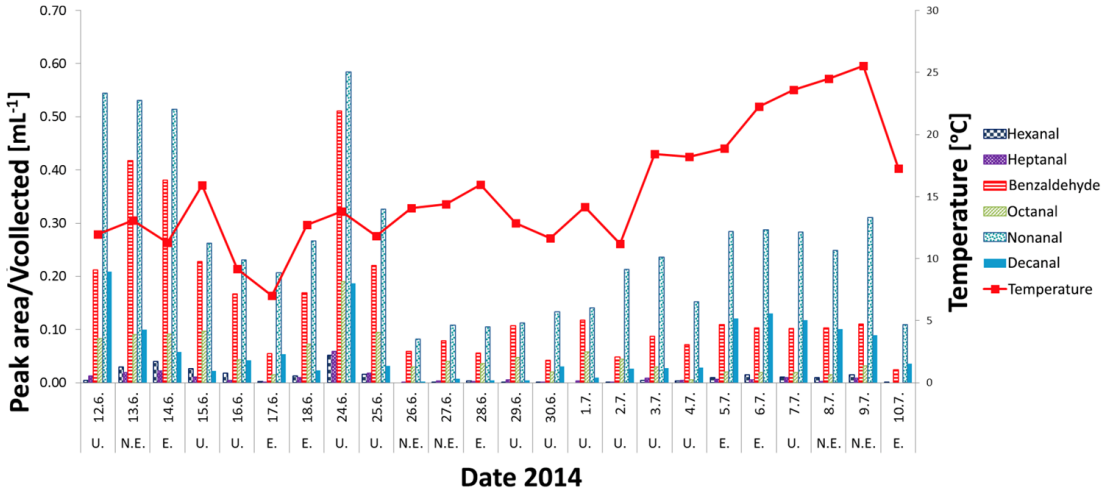
Figure 10. Non-destructive sampling of VOCs emitted by (a) a whole cluster of grapes and (b) a single grape berry on a vine [62]. Adapted from Ref. [62] under Creative Commons Attribution 4.0 License.

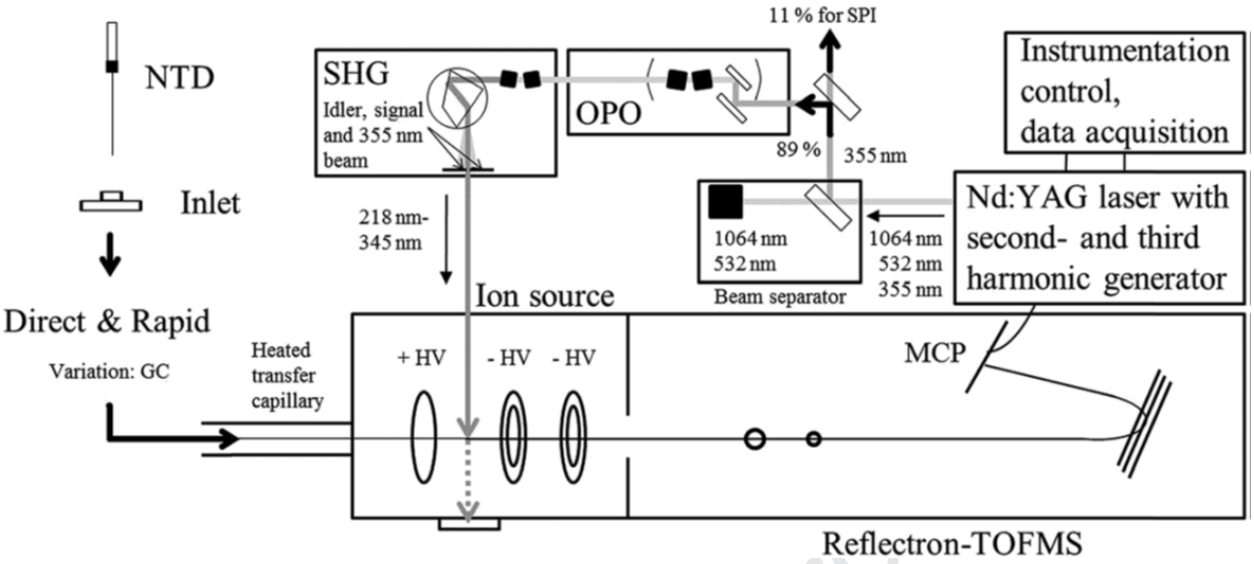


a

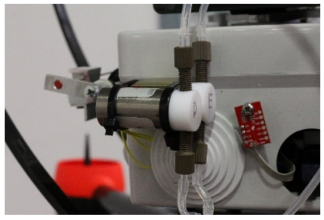

Δ3-carene (GC-MS)
peak area
α-pinene (GC-MS)
peak area
limonene (GC-MS)
peak area
15/06/2013
16/06/2013
17/06/2013
18/06/2013
19/06/2013

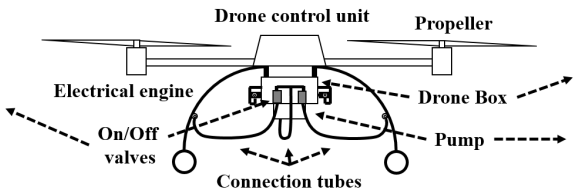
b

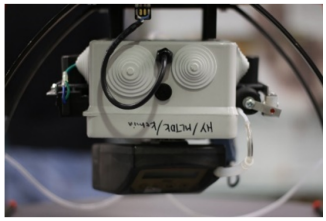

Peak area/Vcollected [mL-1]
Temperature [°C]
Hexanal
Heptanal
Benzaldehyde
Octanal
Nonanal
Decanal
Temperature
Date 2014



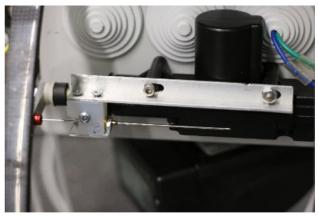
a

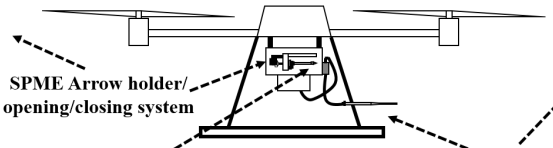


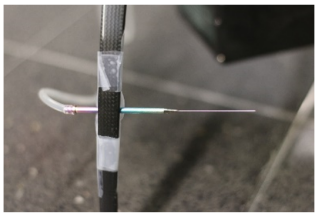

Drone control unit
Propeller
Electrical engine
Drone Box
On/Off valves
Pump
Connection tubes

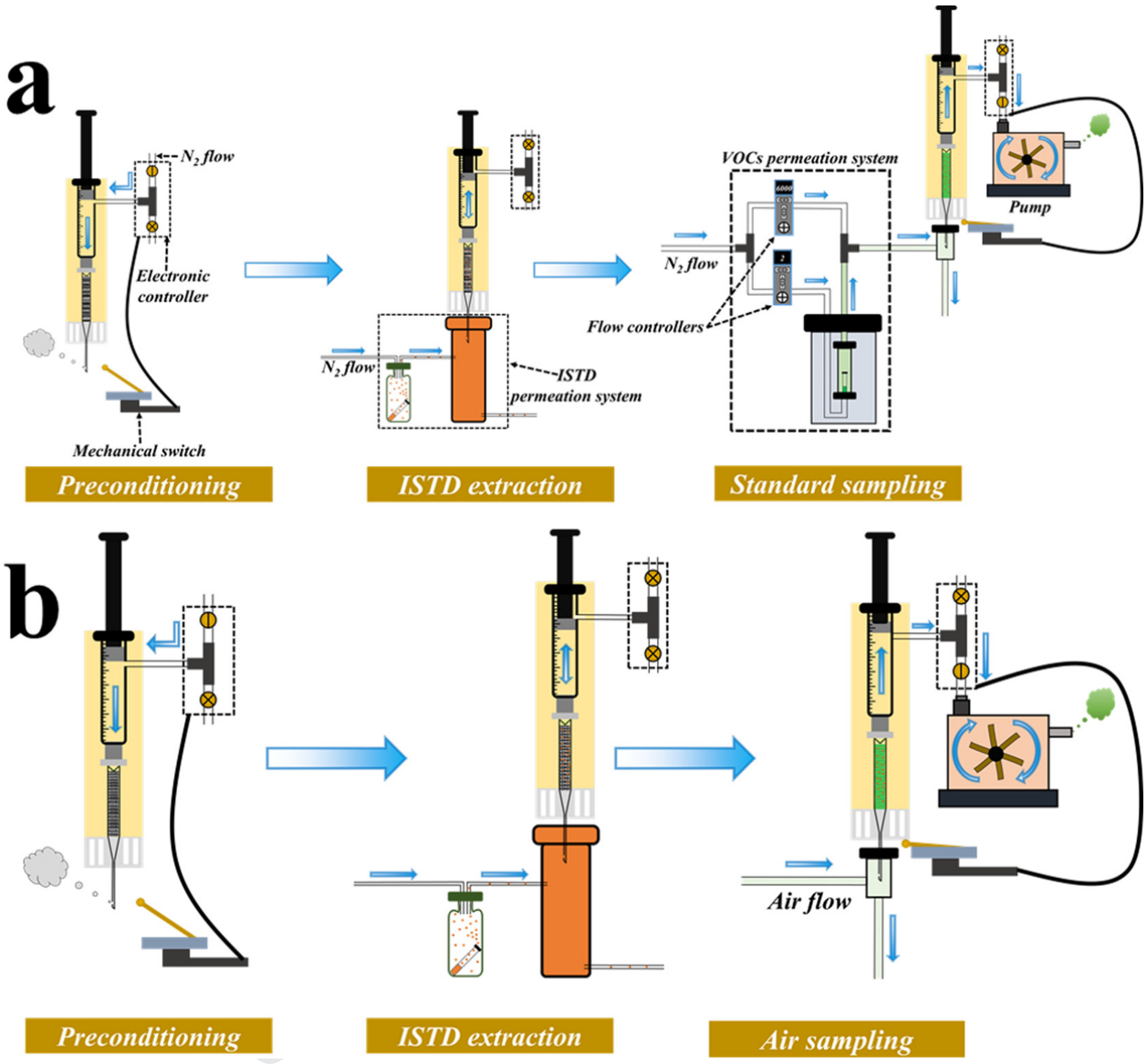


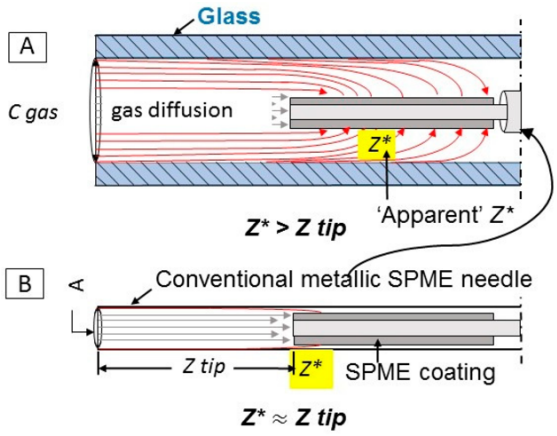
b

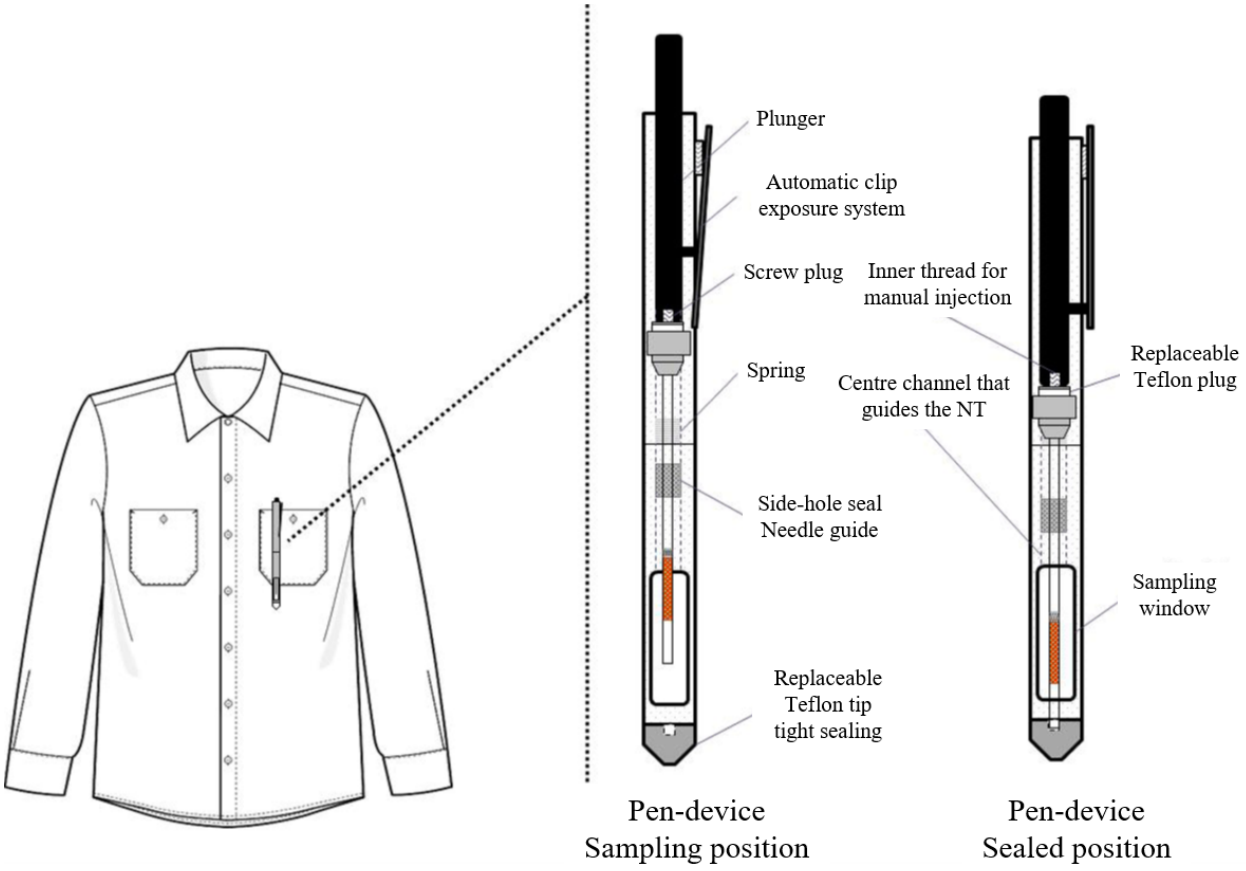


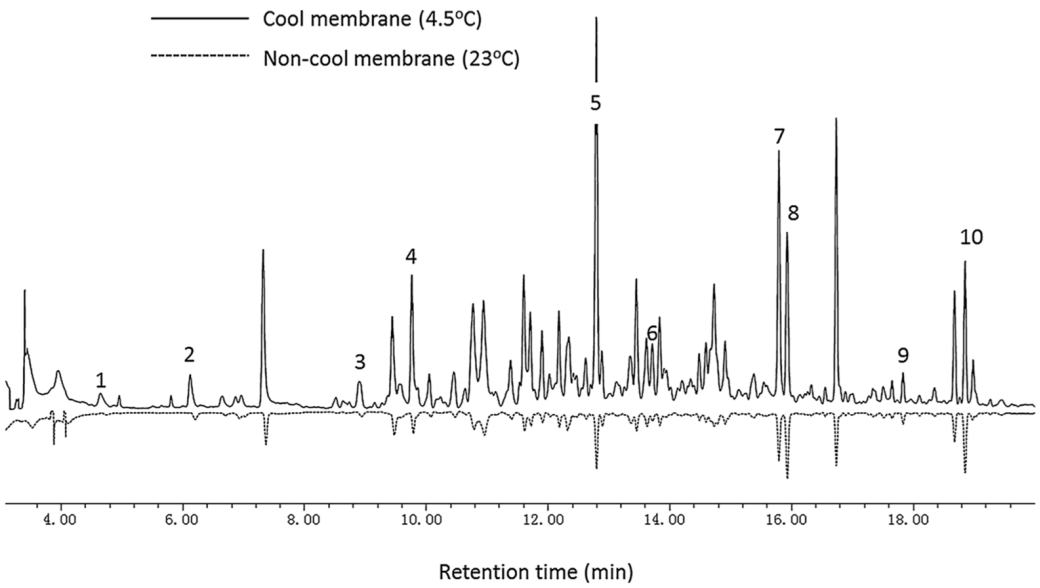

SPME Arrow holder/ opening/closing system
ITEX
SPME Arrow
Coating
Closed
Open
Sorbent bed
Side hole

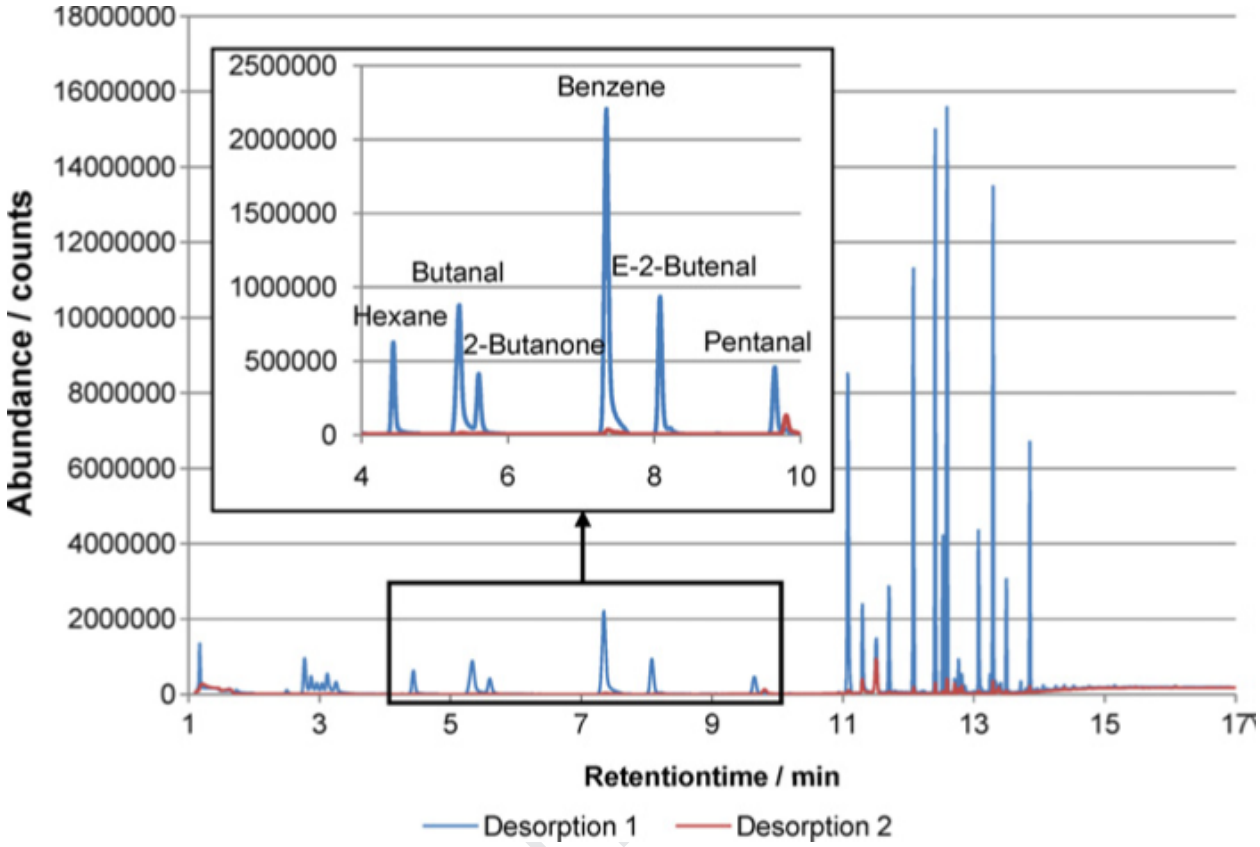


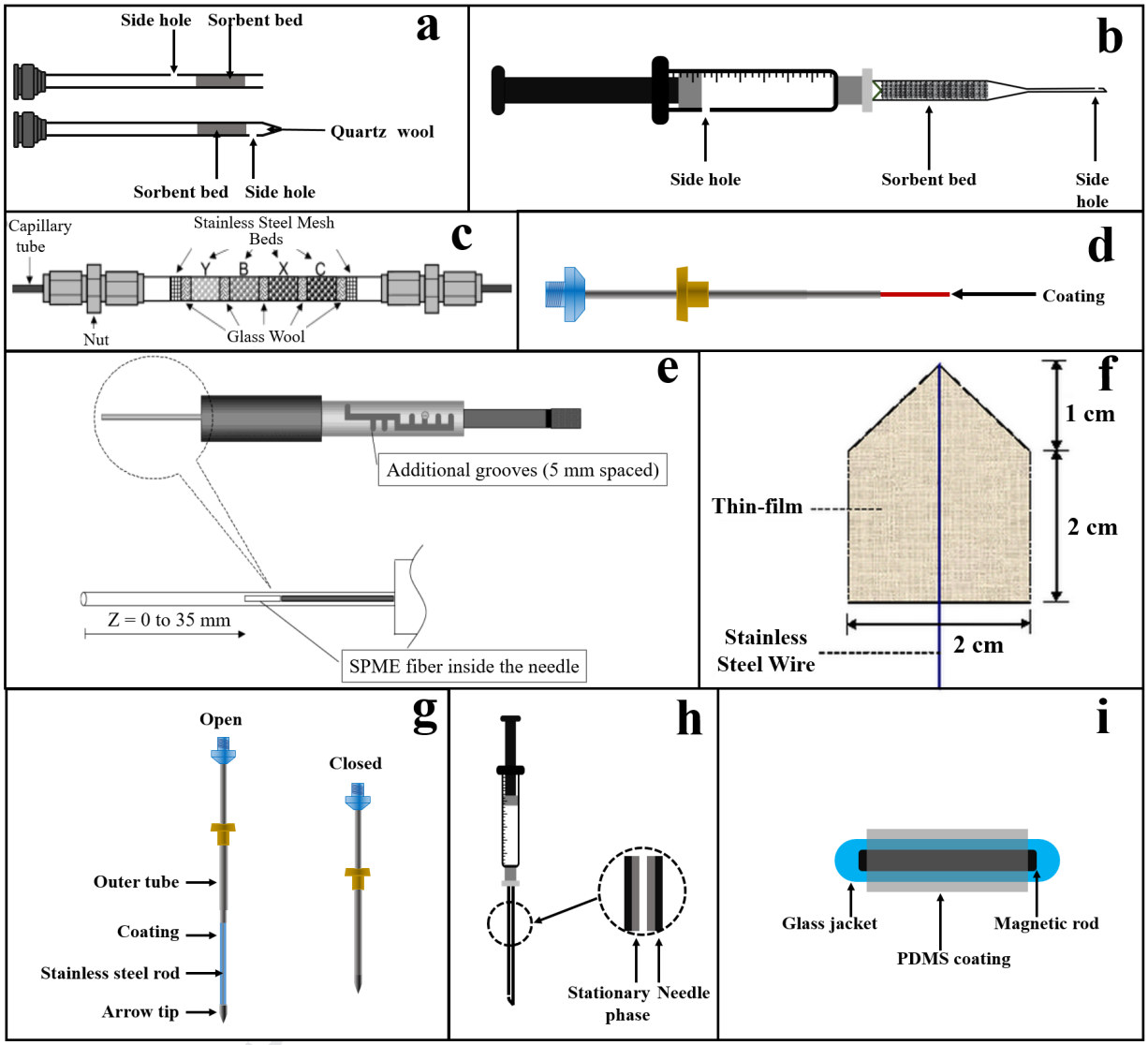

a
N_2 flow
Electronic controller
Mechanical switch
Preconditioning
N_2 flow
ISTD permeation system
ISTD extraction
VOCs permeation system
N_2 flow
Flow controllers
Pump
Standard sampling
b
Preconditioning
ISTD extraction
Air flow
Air sampling




Plunger
Automatic clip exposure system
Screw plug
Inner thread for manual injection
Spring
Centre channel that guides the NT
Replaceable Teflon plug
Side-hole seal Needle guide
Sampling window
Replaceable Teflon tip tight sealing
Pen-device Sampling position
Pen-device Sealed position




Abundance / counts
Retentiontime / min
Benzene
Butanal
E-2-Butenal
Hexane
2-Butanone
Pentanal
Desorption 1
Desorption 2


a
Side hole
Sorbent bed
Quartz wool
Sorbent bed
Side hole
b
Side hole
Sorbent bed
Side hole
c
Capillary tube
Stainless Steel Mesh Beds
Y
B
X
C
Nut
Glass Wool
d
Coating
e
Additional grooves (5 mm spaced)
Z = 0 to 35 mm
SPME fiber inside the needle
f
1 cm
2 cm
Thin-film
Stainless Steel Wire
2 cm
g
Open
Closed
Outer tube
Coating
Stainless steel rod
Arrow tip
h
Stationary phase
Needle
i
Glass jacket
Magnetic rod
PDMS coating

Highlights

- Versatile and flexible microextraction techniques suit well for air sampling
- Integration of passive and active air sampling systems provide more comprehensive data
- Miniaturised, microextraction based air sampling techniques are suitable for field studies
- Miniaturised air sampling is applicable for outdoor, indoor and breath air
- Automation of miniaturised microextraction techniques is easy

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: